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(54) Title: ZIRCONIUM PRETREATMENT COMPOSITIONS CONTAINING LITHIUM, ASSOCIATED METHODS FOR TREATING METAL SUBSTRATES, AND RELATED COATED METAL SUBSTRATES

(57) **Abstract**: Disclosed are pretreatment compositions and associated methods for treating metal substrates with pretreatment compositions, including ferrous substrates, such as cold rolled steel and electrogalvanized steel. The pretreatment composition includes: a Group IIIB and/or IVB metal; free fluoride; and lithium. The methods include contacting the metal substrates with the pretreatment composition.

ZIRCONIUM PRETREATMENT COMPOSITIONS CONTAINING LITHIUM, ASSOCIATED METHODS FOR TREATING METAL SUBSTRATES, AND RELATED COATED METAL SUBSTRATES

FIELD OF THE INVENTION

[0001] The present invention relates to pretreatment compositions and methods for treating a metal substrate, including ferrous substrates such as cold rolled steel and electrogalvanized steel, or aluminum alloys. The present invention also relates to a coated metal substrate.

BACKGROUND OF THE INVENTION

[0002] The use of protective coatings on metal substrates for improved corrosion resistance and paint adhesion is common. Conventional techniques for coating such substrates include techniques that involve pretreating the metal substrate with a phosphate conversion coating and chrome-containing rinses. The use of such phosphate and/or chromate-containing compositions, however, imparts environmental and health concerns.

[0003] As a result, chromate-free and/or phosphate-free pretreatment compositions have been developed. Such compositions are generally based on chemical mixtures that react with the substrate surface and bind to it to form a protective layer. For example, pretreatment compositions based on a Group IIIB or IVB metal compound have recently become more prevalent. Such compositions often contain a source of free fluorine, i.e., fluorine that is isolated in the pretreatment composition as opposed to fluorine that is bound to another element, such as the Group IIIB or IVB metal. Free fluorine can etch the surface of the metal substrate, thereby promoting deposition of a Group IIIB or IVB metal coating. Nevertheless, the corrosion resistance capability of these pretreatment compositions has generally been significantly inferior to conventional phosphate and/or chromium containing pretreatments.

[0004] It would be desirable to provide methods for treating a metal substrate that overcome at least some of the previously described drawbacks of the prior art, including the environmental drawbacks associated with the use of chromates and/or phosphates. It also would be desirable to provide methods for treating metal substrate that imparts corrosion resistance properties that are equivalent to, or even superior to, the corrosion resistance properties imparted through the use of phosphate conversion coatings. It would also be desirable to provide related coated metal substrates.

SUMMARY OF THE INVENTION

[0005] In certain respects, the present invention is directed to a pretreatment composition for treating a metal substrate comprising: a Group IIIB and/or Group IVB metal; free fluoride; and lithium.

[0006] In still other respects, the present invention is directed to a method for treating a metal substrate comprising contacting the metal substrate with a pretreatment composition comprising a Group IIIB and/or Group IVB metal, free fluoride, and lithium.

[0007] In still other respects, the present invention is directed to a method of coating a metal substrate comprising electrophoretically depositing a coating composition onto the metal substrate, wherein the metal substrate comprises a treated surface layer comprising a Group IIIB and/or Group IVB metal, free fluoride, and lithium.

[0008] In still other respects, the present invention is directed to a pretreated metal substrate comprising a surface layer comprising a Group IVB metal, free fluoride, and lithium on at least a portion of the substrate.

[0009] In still other respects, the present invention is directed to an electrophoretically coated metal substrate comprising: a treated surface layer comprising a Group IIIB and/or Group IVB metal, free fluoride, and lithium on a surface of the metal substrate; and an electrophoretically deposited coating over at least a portion of the treated surface layer.

DETAILED DESCRIPTION

[0010] For purposes of the following detailed description, it is to be understood that the invention may assume various alternative variations and step sequences, except where expressly specified to the contrary. Moreover, other than in any operating examples, or where otherwise indicated, all numbers expressing, for example, quantities of ingredients used in the specification and claims are to be understood as being modified in all instances by the term "about". Accordingly, unless indicated to the contrary, the numerical parameters set forth in the following specification and attached claims are approximations that may vary depending upon the desired properties to be obtained by the present invention. At the very least, and not as an attempt to limit the application of the doctrine of equivalents to the scope of the claims, each numerical parameter should at least be construed in light of the number of reported significant digits and by applying ordinary rounding techniques.

[0011] Notwithstanding that the numerical ranges and parameters setting forth the broad scope of the invention are approximations, the numerical values set forth in the specific examples are reported as precisely as possible. Any numerical value, however, inherently contains certain errors necessarily resulting from the standard variation found in their respective testing measurements.

[0012] Also, it should be understood that any numerical range recited herein is intended to include all sub-ranges subsumed therein. For example, a range of "1 to 10" is intended to include all sub-ranges between (and including) the recited minimum value of 1 and the recited maximum value of 10, that is, having a minimum value equal to or greater than 1 and a maximum value of equal to or less than 10.

[0013] In this application, the use of the singular includes the plural and plural encompasses singular, unless specifically stated otherwise. In addition, in this application, the use of "or" means "and/or" unless specifically stated otherwise, even though "and/or" may be explicitly used in certain instances.

[0014] Unless otherwise disclosed herein, as used herein, the term “substantially free” means that a particular material is not purposefully added to a composition and only is present in trace amounts or as an impurity. As used herein, the term "completely free" means that a composition does not comprise a particular material. That is, the composition comprises 0 weight percent of such material.

[0015] Certain embodiments of the pretreatment composition are directed to a pretreatment composition for treating a metal substrate comprising a Group IIIB and/or Group IVB metal, free fluoride, and lithium. In certain embodiments, the pretreatment composition may be substantially free of phosphates and/or chromates. The treatment of the metal substrate with the pretreatment composition results in improved corrosion resistance of the substrate compared to substrates that have not been pretreated with the pretreated composition without requiring phosphates or chromates. Inclusion of lithium and/or lithium in combination with molybdenum in the pretreatment composition may provide improved corrosion performance on steel and steel substrates.

[0016] Certain embodiments of the present invention are directed to compositions and methods for treating a metal substrate. Suitable metal substrates for use in the present invention include those that are often used in the assembly of automotive bodies, automotive parts, and other articles, such as small metal parts, including fasteners, i.e., nuts, bolts, screws, pins, nails, clips, buttons, and the like. Specific examples of suitable metal substrates include, but are not limited to, cold rolled steel, hot rolled steel, steel coated with zinc metal, zinc compounds, or zinc alloys, such as electrogalvanized steel, hot-dipped galvanized steel, galvanealed steel, and steel plated with zinc alloy. Also, aluminum alloys, aluminum plated steel and aluminum alloy plated steel substrates may be used. Other suitable non-ferrous metals include copper and magnesium, as well as alloys of these materials. Moreover, the metal substrate being treated by the methods of the present invention may be a cut edge of a substrate that is otherwise treated and/or coated over the rest of its surface. The metal substrate treated in accordance with the methods of the present invention may be in the form of, for example, a sheet of metal or a fabricated part.

[0017] The substrate to be treated in accordance with the methods of the present invention may first be cleaned to remove grease, dirt, or other extraneous matter. This is often done by employing mild or strong alkaline cleaners, such as are commercially available and conventionally used in metal pretreatment processes. Examples of alkaline cleaners suitable for use in the present invention include Chemkleen 163, Chemkleen 166M/C, Chemkleen 490MX, Chemkleen 2010LP, Chemkleen 166 HP, Chemkleen 166 M, Chemkleen 166 M/Chemkleen 171/11, each of which are commercially available from PPG Industries, Inc. Such cleaners are often followed and/or preceded by a water rinse.

[0018] In certain embodiments, prior to the pretreatment step, the substrate may be contacted with a pre-rinse solution. Pre-rinse solutions, in general, may utilize certain solubilized metal ions or other inorganic materials (such as phosphates or simple or complex fluorides or acids) to enhance the corrosion protection of pretreated metal substrates. Suitable non-chrome pre-rinse solutions that may be utilized in the present invention are disclosed in U.S. Patent Application No. 2010/0159258A1, assigned to PPG Industries, Inc. and herein incorporated by reference.

[0019] Certain embodiments of the present invention are directed to methods for treating a metal substrate, with or without the optional pre-rinse, that comprise contacting the metal substrate with a pretreatment composition comprising a Group IIIB and/or IVB metal. As used herein, the term "pretreatment composition" refers to a composition that, upon contact with the substrate, reacts with and chemically alters the substrate surface and binds to it to form a protective layer.

[0020] The pretreatment composition may comprise a carrier, often an aqueous medium, so that the composition is in the form of a solution or dispersion of a Group IIIB or IVB metal compound in the carrier. In these embodiments, the solution or dispersion may be brought into contact with the substrate by any of a variety of known techniques, such as dipping or immersion, spraying, intermittent spraying, dipping followed by spraying, spraying followed by dipping, brushing, or roll-coating. In certain embodiments, the solution or dispersion when applied to the metal substrate is at a temperature ranging from 60 to 185°F (15 to85°C). For example, the pretreatment process may be carried out at ambient or room temperature. The contact time is often from 10 seconds to 5 minutes, such as 30 seconds to 2 minutes.

[0021] As used herein, the term "Group IIIB and/or IVB metal" refers to an element that is in Group IIIB or Group IVB of the CAS Periodic Table of the Elements. Where applicable, the metal themselves may be used. In certain embodiments, Group IIIB and/or Group IVB metal compounds are used. As used herein, the term "Group IIIB and/or IVB metal compound" refers to compounds that include at least one element that is in Group IIIB or Group IVB of the CAS Period Table of the Elements.

[0022] In certain embodiments, the Group IIIB and/or IVB metal compound used in the pretreatment composition is a compound of zirconium, titanium, hafnium, yttrium, cerium, or a mixture thereof. Suitable compounds of zirconium include, but are not limited to, hexafluorozirconic acid, alkali metal and ammonium salts thereof, ammonium zirconium carbonate, zirconyl nitrate, zirconyl sulfate, zirconium carboxylates and zirconium hydroxy carboxylates, such as hydrofluorozirconic acid, zirconium acetate, zirconium oxalate, ammonium zirconium glycolate, ammonium zirconium lactate, ammonium zirconium citrate, and mixtures thereof. Suitable compounds of titanium include, but are not limited to, fluorotitanic acid and its salts. A suitable compound of hafnium includes, but is not limited to, hafnium nitrate. A suitable compound of yttrium includes, but is not limited to, yttrium nitrate. A suitable compound of cerium includes, but is not limited to, cerous nitrate.

[0023] In certain embodiments, the Group IIIB and/or IVB metal is present in the pretreatment composition in an amount of 50 to 500 parts per million ("ppm") metal, such as 75 to 250 ppm, based on the total weight of all of the ingredients in the pretreatment composition. The amount of Group IIIB and/or IVB metal in the pretreatment composition can range between the recited values inclusive of the recited values.

[0024] The pretreatment compositions also comprise free fluoride. The source of free fluoride in the pretreatment compositions of the present invention can vary. For example, in some cases, the free fluoride may derive from the Group IIIB and/or IVB metal compound used in the pretreatment composition, such as is the case, for example, with hexafluorozirconic acid. As the Group IIIB and/or IVB metal is deposited upon the metal substrate during the pretreatment process, fluorine in the hexafluorozirconic acid will become free fluoride and the level of free fluoride in the pretreatment composition will, if left unchecked, increase with time as metal is pretreated with the pretreatment composition of the present invention.

[0025] In addition, the source of free fluoride in the pretreatment compositions of the present invention may include a compound other than the Group IIIB and/or IVB metal compound. Non-limiting examples of such sources include HF, NH_4F, NH_4HF_2, NaF, and $NaHF_2$. As used herein, the term "free fluoride" refers to isolated fluoride ions. In certain embodiments, the free fluoride is present in the pretreatment composition in an amount of 5 to 250 ppm, such as 25 to 100 ppm, based on the total weight of the ingredients in the pretreatment composition. The amount of free fluoride in the pretreatment composition can range between the recited values inclusive of the recited values.

[0026] In certain embodiments, a K ratio of a compound (A) containing a Group IIIB and/or Group IVB metal in mole weight to a compound (B) containing fluorine as a supplying source of free fluoride in mole weight calculated as HF has a ratio of $K=A/B$, where $K>0.10$. In certain embodiments, $0.11<K<0.25$.

[0027] The pretreatment compositions also comprise lithium. In certain embodiments, the source of lithium used in the pretreatment composition is in the form of a salt. Suitable lithium salts are lithium nitrate, lithium sulfate, lithium fluoride, lithium chloride, lithium hydroxide, lithium carbonate, and lithium iodide. In certain embodiments, the inclusion of lithium in the pretreatment composition results in improved corrosion resistance of steel and steel substrates.

[0028] In certain embodiments, the lithium is present in the pretreatment composition in an amount of 5 to 500 ppm, such as 25 to 125 ppm, based on the total weight of the ingredients in the pretreatment composition. In certain embodiments, the lithium is present in the pretreatment composition in an amount of less than 200 ppm. The amount of lithium in the pretreatment composition can range between the recited values inclusive of the recited values.

[0029] In certain embodiments, the molar ratio of the Group IIIB and/or IVB metal to the lithium is between 100:1 and 1:100, for example, between 12:1 and 1:50.

[0030] In certain embodiments, the pretreatment compositions also comprise an electropositive metal. As used herein, the term "electropositive metal" refers to metals that are more electropositive than the metal substrate. This means that, for purposes of the present invention, the term "electropositive metal" encompasses metals that are less easily oxidized than the metal of the metal substrate that is being treated. As will be appreciated by those skilled in the art, the tendency of a metal to be oxidized is called the oxidation potential, is expressed in volts, and is measured relative to a standard hydrogen electrode, which is arbitrarily assigned an oxidation potential of zero. The oxidation potential for several elements is set forth in Table 1 below. An element is less easily oxidized than another element if it has a voltage value, E*, in the following table, that is greater than the element to which it is being compared.

Table 1

Element	Half-cell reaction	Voltage, E*
Potassium	$K^+ + e \rightarrow K$	-2.93
Calcium	$Ca^{2+} + 2e \rightarrow Ca$	-2.87
Sodium	$Na^+ + e \rightarrow Na$	-2.71
Magnesium	$Mg^{2+} + 2e \rightarrow Mg$	-2.37
Aluminum	$Al^{3+} + 3e \rightarrow Al$	-1.66
Zinc	$Zn^{2+} + 2e \rightarrow Zn$	-0.76
Iron	$Fe^{2+} + 2e \rightarrow Fe$	-0.44
Nickel	$Ni^{2+} + 2e \rightarrow Ni$	-0.25
Tin	$Sn^{2+} + 2e \rightarrow Sn$	-0.14
Lead	$Pb^{2+} + 2e \rightarrow Pb$	-0.13

Hydrogen	$2H^+ + 2e \rightarrow H_2$	-0.00
Copper	$Cu^{2+} + 2e \rightarrow Cu$	0.34
Mercury	$Hg_2^{2+} + 2e \rightarrow 2Hg$	0.79
Silver	$Ag^+ + e \rightarrow Ag$	0.80
Gold	$Au^{3+} + 3e \rightarrow Au$	1.50

[0031] Thus, as will be apparent, when the metal substrate comprises one of the materials listed earlier, such as cold rolled steel, hot rolled steel, steel coated with zinc metal, zinc compounds, or zinc alloys, hot-dipped galvanized steel, galvanealed steel, steel plated with zinc alloy, aluminum alloys, aluminum plated steel, aluminum alloy plated steel, magnesium and magnesium alloys, suitable electropositive metals for deposition thereon include, for example, nickel, copper, silver, and gold, as well mixtures thereof.

[0032] In certain embodiments in which the electropositive metal comprises copper, both soluble and insoluble compounds may serve as the source of copper in the pretreatment compositions. For example, the supplying source of copper ions in the pretreatment composition may be a water soluble copper compound. Specific examples of such materials include, but are not limited to, copper cyanide, copper potassium cyanide, copper sulfate, copper nitrate, copper pyrophosphate, copper thiocyanate, disodium copper ethylenediaminetetraacetate tetrahydrate, copper bromide, copper oxide, copper hydroxide, copper chloride, copper fluoride, copper gluconate, copper citrate, copper lauroyl sarcosinate, copper formate, copper acetate, copper propionate, copper butyrate, copper lactate, copper oxalate, copper phytate, copper tartarate, copper malate, copper succinate, copper malonate, copper maleate, copper benzoate, copper salicylate, copper aspartate, copper glutamate, copper fumarate, copper glycerophosphate, sodium copper chlorophyllin, copper fluorosilicate, copper fluoroborate and copper iodate, as well as copper salts of carboxylic acids in the homologous series formic acid to decanoic acid, copper salts of polybasic acids in the series oxalic acid to suberic acid, and copper salts of hydroxycarboxylic acids, including glycolic, lactic, tartaric, malic and citric acids.

[0033] When copper ions supplied from such a water-soluble copper compound are precipitated as an impurity in the form of copper sulfate, copper oxide, etc., it may be desirable to add a complexing agent that suppresses the precipitation of copper ions, thus stabilizing them as a copper complex in the solution.

[0034] In certain embodiments, the copper compound is added as a copper complex salt such as $K_3Cu(CN)_4$ or Cu-EDTA, which can be present stably in the pretreatment composition on its own, but it is also possible to form a copper complex that can be present stably in the pretreatment composition by combining a complexing agent with a compound that is difficultly soluble on its own. Examples thereof include a copper cyanide complex formed by a combination of CuCN and KCN or a combination of CuSCN and KSCN or KCN, and a Cu-EDTA complex formed by a combination of $CuSO_4$ and EDTA•2Na.

[0035] With regard to the complexing agent, a compound that can form a complex with copper ions can be used; examples thereof include inorganic compounds such as cyanide compounds and thiocyanate compounds, and polycarboxylic acids, and specific examples thereof include ethylenediaminetetraacetic acid, salts of ethylenediaminetetraacetic acid such as dihydrogen disodium ethylenediaminetetraacetate dihydrate, aminocarboxylic acids such as nitrilotriacetic acid and iminodiacetic acid, oxycarboxylic acids such as citric acid and tartaric acid, succinic acid, oxalic acid, ethylenediaminetetramethylenephosphonic acid, and glycine.

[0036] In certain embodiments, the electropositive metal is present in the pretreatment composition in an amount of less than 100 ppm, such as 1 or 2 ppm to 35 or 40 ppm, based on the total weight of all of the ingredients in the pretreatment composition. The amount of electropositive metal in the pretreatment composition can range between the recited values inclusive of the recited values.

[0037] In certain embodiments, the pretreatment compositions may also comprise molybdenum. In certain embodiments, the source of molybdenum used in the pretreatment composition is in the form of a salt. Suitable molybdenum salts are sodium molybdate, calcium molybdate, potassium molybdate, ammonium molybdate, molybdenum chloride, molybdenum acetate, molybdenum sulfamate, molybdenum formate, or molybdenum lactate.

[0038] In certain embodiments, the molybdenum is present in the pretreatment composition in an amount of 5 to 500 ppm, such as 5 to 150 ppm, based on the total weight of the ingredients in the pretreatment composition. The amount of molybdenum in the pretreatment composition can range between the recited values inclusive of the recited values.

[0039] In certain embodiments, the pH of the pretreatment composition ranges from 1 to 6, such as from 2 to 5.5. The pH of the pretreatment composition may be adjusted using, for example, any acid or base as is necessary. In certain embodiments, the pH of the solution is maintained through the inclusion of a basic material, including water soluble and/or water dispersible bases, such as sodium hydroxide, sodium carbonate, potassium hydroxide, ammonium hydroxide, ammonia, and/or amines such as triethylamine, methylethyl amine, or mixtures thereof.

[0040] In certain embodiments, the pretreatment composition also may comprise a resinous binder. Suitable resins include reaction products of one or more alkanolamines and an epoxy-functional material containing at least two epoxy groups, such as those disclosed in United States Patent No. 5,653,823. In some cases, such resins contain beta hydroxy ester, imide, or sulfide functionality, incorporated by using dimethylolpropionic acid, phthalimide, or mercaptoglycerine as an additional reactant in the preparation of the resin. Alternatively, the reaction product is that of the diglycidyl ether of Bisphenol A (commercially available from Shell Chemical Company as EPON 880), dimethylol propionic acid, and diethanolamine in a 0.6 to 5.0:0.05 to 5.5:1 mole ratio. Other suitable resinous binders include water soluble and water dispersible polyacrylic acids as disclosed in United States Patent Nos. 3,912,548 and 5,328,525; phenol formaldehyde resins as described in United States Patent Nos. 5,662,746; water soluble polyamides such as those disclosed in WO 95/33869; copolymers of maleic or acrylic acid with allyl ether as described in Canadian patent application 2,087,352; and water soluble and dispersible resins including epoxy resins, aminoplasts, phenol-formaldehyde resins, tannins, and polyvinyl phenols as discussed in United States Patent No. 5,449,415.

[0041] In these embodiments of the present invention, the resinous binder often may be present in the pretreatment composition in an amount of 0.005 percent to 30 percent by weight, such as 0.5 to 3 percent by weight, based on the total weight of the ingredients in the composition.

[0042] In other embodiments, however, the pretreatment composition may be substantially free or, in some cases, completely free of any resinous binder. As used herein, the term "substantially free", when used with reference to the absence of resinous binder in the pretreatment composition, means that any resinous binder is present in the pretreatment composition in a trace amount of less than 0.005 percent by weight. As used herein, the term "completely free" means that there is no resinous binder in the pretreatment composition at all.

[0043] The pretreatment composition may optionally contain other materials such as nonionic surfactants and auxiliaries conventionally used in the art of pretreatment. In an aqueous medium, water dispersible organic solvents, for example, alcohols with up to about 8 carbon atoms such as methanol, isopropanol, and the like, may be present; or glycol ethers such as the monoalkyl ethers of ethylene glycol, diethylene glycol, or propylene glycol, and the like. When present, water dispersible organic solvents are typically used in amounts up to about ten percent by volume, based on the total volume of aqueous medium.

[0044] Other optional materials include surfactants that function as defoamers or substrate wetting agents. Anionic, cationic, amphoteric, and/or nonionic surfactants may be used. Defoaming surfactants are often present at levels up to 1 weight percent, such as up to 0.1 percent by weight, and wetting agents are typically present at levels up to 2 percent, such as up to 0.5 percent by weight, based on the total weight of the pretreatment composition.

[0045] In certain embodiments, the pretreatment composition also may comprise a silane, such as, for example, an amino group-containing silane coupling agent, a hydrolysate thereof, or a polymer thereof, as described in United States Patent Application Publication No. 2004/0163736 A1 at [0025] to [0031], the cited portion of which being incorporated herein by reference. In other embodiments of the present invention, however, the pretreatment composition is substantially free, or, in some cases, completely free of any such amino group-containing silane coupling agent. As used herein, the term "substantially free", when used with reference to the absence of amino-group containing silane coupling agent in the pretreatment composition, means that any amino-group containing silane coupling agent, hydrolysate thereof, or polymer thereof that is present in the pretreatment composition is present in a trace amount of less than 5 ppm. As used herein, the term "completely free" means that there is no amino-group containing silane coupling agent, hydrolysate thereof, or polymer thereof in the pretreatment composition at all.

[0046] In certain embodiments, the pretreatment composition also may comprise a reaction accelerator, such as nitrite ions, nitro-group containing compounds, hydroxylamine sulfate, persulfate ions, sulfite ions, hyposulfite ions, peroxides, iron (III) ions, citric acid iron compounds, bromate ions, perchlorinate ions, chlorate ions, chlorite ions as well as ascorbic acid, citric acid, tartaric acid, malonic acid, succinic acid and salts thereof. Specific examples of suitable materials and their amounts are described in United States Patent Application Publication No. 2004/0163736 A1 at [0032] to [0041], the cited portion of which being incorporated herein by reference.

[0047] In certain embodiments, the pretreatment composition is substantially or, in some cases, completely free of phosphate ions. As used herein, the term "substantially free," when used in reference to the absence of phosphate ions in the pretreatment composition, means that phosphate ions are not present in the composition to such an extent that the phosphate ions cause a burden on the environment. For example, phosphate ions may be present in the pretreatment composition in a trace amount of less than 10 ppm. That is, phosphate ions are not substantially used and the formation of sludge, such as iron phosphate and zinc phosphate, formed in the case of using a treating agent based on zinc phosphate, is eliminated.

[0048] In certain embodiments, the pretreatment composition also may include a source of phosphate ions. For example, phosphate ions may be added in an amount of greater than 10 ppm up to 60 ppm, such as for example 20 ppm to 40 ppm or for example 30 ppm.

[0049] In certain embodiments, the pretreatment composition is substantially, or in some cases, completely free of chromate. As used herein, the term "substantially free," when used in reference to the absence of chromate in the pretreatment composition, means that any chromate is present in the pretreatment composition in a trace amount of less than 5 ppm. As used herein, the term "completely free," when used in reference to the absence of chromate in the pretreatment composition, means that there is no chromate in the pretreatment composition at all.

[0050] In certain embodiments, the film coverage of the residue of the pretreatment coating composition generally ranges from 1 to 1000 milligrams per square meter (mg/m^2), for example, from 10 to 400 mg/m^2. In certain embodiments, the thickness of the pretreatment coating may be less than 1 micrometer, for example from 1 to 500 nanometers, or from 10 to 300 nanometers. Following contact with the pretreatment solution, the substrate optionally may be rinsed with water and dried. In certain embodiments, the substrate may be dried for 0.5 to 30 minutes in an oven at 15 to 200°C (60 to 400 °F), such as for 10 minutes at 70°F.

[0051] Optionally, after the pretreatment step, the substrate may then be contacted with a post-rinse solution. Post-rinse solutions, in general, utilize certain solubilized metal ions or other inorganic materials (such as phosphates or simple or complex fluorides) to enhance the corrosion protection of pretreated metal substrates. These post-rinse solutions may be chrome containing or non-chrome containing post-rinse solutions. Suitable non-chrome post-rinse solutions that may be utilized in the present invention are disclosed in U.S. Patents 5,653,823; 5,209,788; and 5,149,382; all assigned to PPG Industries, Inc. and herein incorporated by reference. In addition, organic materials (resinous or otherwise) such as phosphitized epoxies, base-solubilized, carboxylic acid containing polymers, at least partially neutralized interpolymers of hydroxyl-alkyl esters of unsaturated carboxylic acids, and amine salt-group containing resins (such as acid-solubilized reaction products of polyepoxides and primary or secondary amines) may also be utilized alone or in combination with solubilized metal ions and/or other inorganic materials. After the optional post-rinse (when utilized), the substrate may be rinsed with water prior to subsequent processing.

[0052] In certain embodiments of the methods of the present invention, after the substrate is contacted with the pretreatment composition, it then may be contacted with a coating composition comprising a film-forming resin. Any suitable technique may be used to contact the substrate with such a coating composition, including, for example, brushing, dipping, flow coating, spraying and the like. In certain embodiments, however, as described in more detail below, such contacting comprises an electrocoating step wherein an electrodepositable composition is deposited onto the metal substrate by electrodeposition.

[0053] As used herein, the term "film-forming resin" refers to resins that can form a self-supporting continuous film on at least a horizontal surface of a substrate upon removal of any diluents or carriers present in the composition or upon curing at ambient or elevated temperature. Conventional film-forming resins that may be used include, without limitation, those typically used in automotive OEM coating compositions, automotive refinish coating compositions, industrial coating compositions, architectural coating compositions, coil coating compositions, and aerospace coating compositions, among others.

[0054] In certain embodiments, the coating composition comprises a thermosetting film-forming resin. As used herein, the term "thermosetting" refers to resins that "set" irreversibly upon curing or crosslinking, wherein the polymer chains of the polymeric components are joined together by covalent bonds. This property is usually associated with a cross-linking reaction of the composition constituents often induced, for example, by heat or radiation. Curing or crosslinking reactions also may be carried out under ambient conditions. Once cured or crosslinked, a thermosetting resin will not melt upon the application of heat and is insoluble in solvents. In other embodiments, the coating composition comprises a thermoplastic film-forming resin. As used herein, the term "thermoplastic" refers to resins that comprise polymeric components that are not joined by covalent bonds and thereby can undergo liquid flow upon heating and are soluble in solvents.

[0055] As previously indicated, in certain embodiments, the substrate is contacted with a coating composition comprising a film-forming resin by an electrocoating step wherein an electrodepositable composition is deposited onto the metal substrate by electrodeposition. In the process of electrodeposition, the metal substrate being treated, serving as an electrode, and an electrically conductive counter electrode are placed in contact with an ionic, electrodepositable composition. Upon passage of an electric current between the electrode and counter electrode while they are in contact with the electrodepositable composition, an adherent film of the electrodepositable composition will deposit in a substantially continuous manner on the metal substrate.

[0056] Electrodeposition is usually carried out at a constant voltage in the range of from 1 volt to several thousand volts, typically between 50 and 500 volts. Current density is usually between 1.0 ampere and 15 amperes per square foot (10.8 to 161.5 amperes per square meter) and tends to decrease quickly during the electrodeposition process, indicating formation of a continuous self-insulating film.

[0057] The electrodepositable composition utilized in certain embodiments of the present invention often comprises a resinous phase dispersed in an aqueous medium wherein the resinous phase comprises: (a) an active hydrogen group-containing ionic electrodepositable resin, and (b) a curing agent having functional groups reactive with the active hydrogen groups of (a).

[0058] In certain embodiments, the electrodepositable compositions utilized in certain embodiments of the present invention contain, as a main film-forming polymer, an active hydrogen-containing ionic, often cationic, electrodepositable resin. A wide variety of electrodepositable film-forming resins are known and can be used in the present invention so long as the polymers are "water dispersible," i.e., adapted to be solubilized, dispersed or emulsified in water. The water dispersible polymer is ionic in nature, that is, the polymer will contain anionic functional groups to impart a negative charge or, as is often preferred, cationic functional groups to impart a positive charge.

[0059] Examples of film-forming resins suitable for use in anionic electrodepositable compositions are base-solubilized, carboxylic acid containing polymers, such as the reaction product or adduct of a drying oil or semi-drying fatty acid ester with a dicarboxylic acid or anhydride; and the reaction product of a fatty acid ester, unsaturated acid or anhydride and any additional unsaturated modifying materials which are further reacted with polyol. Also suitable are the at least partially neutralized interpolymers of hydroxy-alkyl esters of unsaturated carboxylic acids, unsaturated carboxylic acid and at least one other ethylenically unsaturated monomer. Still another suitable electrodepositable film-forming resin comprises an alkyd-aminoplast vehicle, i.e., a vehicle containing an alkyd resin and an amine-aldehyde resin. Yet another anionic electrodepositable resin composition comprises mixed esters of a resinous polyol, such as is described in United States Patent No. 3,749,657 at col. 9, lines 1 to 75 and col. 10, lines 1 to 13, the cited portion of which being incorporated herein by reference. Other acid functional polymers can also be used, such as phosphatized polyepoxide or phosphatized acrylic polymers as are known to those skilled in the art.

[0060] As aforementioned, it is often desirable that the active hydrogen-containing ionic electrodepositable resin (a) is cationic and capable of deposition on a cathode. Examples of such cationic film-forming resins include amine salt group-containing resins, such as the acid-solubilized reaction products of polyepoxides and primary or secondary amines, such as those described in United States Patent Nos. 3,663,389; 3,984,299; 3,947,338; and 3,947,339. Often, these amine salt group-containing resins are used in combination with a blocked isocyanate curing agent. The isocyanate can be fully blocked, as described in United States Patent No. 3,984,299, or the isocyanate can be partially blocked and reacted with the resin backbone, such as is described in United States Patent No. 3,947,338. Also, one-component compositions as described in United States Patent No. 4,134,866 and DE-

OS No. 2,707,405 can be used as the film-forming resin. Besides the epoxy-amine reaction products, film-forming resins can also be selected from cationic acrylic resins, such as those described in United States Patent Nos. 3,455,806 and 3,928,157.

[0061] Besides amine salt group-containing resins, quaternary ammonium salt group-containing resins can also be employed, such as those formed from reacting an organic polyepoxide with a tertiary amine salt as described in United States Patent Nos. 3,962,165; 3,975,346; and 4,001,101. Examples of other cationic resins are ternary sulfonium salt group-containing resins and quaternary phosphonium salt-group containing resins, such as those described in United States Patent Nos. 3,793,278 and 3,984,922, respectively. Also, film-forming resins which cure via transesterification, such as described in European Application No. 12463 can be used. Further, cationic compositions prepared from Mannich bases, such as described in United States Patent No. 4,134,932, can be used.

[0062] In certain embodiments, the resins present in the electrodepositable composition are positively charged resins which contain primary and/or secondary amine groups, such as described in United States Patent Nos. 3,663,389; 3,947,339; and 4,116,900. In United States Patent No. 3,947,339, a polyketimine derivative of a polyamine, such as diethylenetriamine or triethylenetetraamine, is reacted with a polyepoxide. When the reaction product is neutralized with acid and dispersed in water, free primary amine groups are generated. Also, equivalent products are formed when polyepoxide is reacted with excess polyamines, such as diethylenetriamine and triethylenetetraamine, and the excess polyamine vacuum stripped from the reaction mixture, as described in United States Patent Nos. 3,663,389 and 4,116,900.

[0063] In certain embodiments, the active hydrogen-containing ionic electrodepositable resin is present in the electrodepositable composition in an amount of 1 to 60 percent by weight, such as 5 to 25 percent by weight, based on total weight of the electrodeposition bath.

[0064] As indicated, the resinous phase of the electrodepositable composition often further comprises a curing agent adapted to react with the active hydrogen groups of the ionic electrodepositable resin. For example, both blocked organic polyisocyanate and aminoplast curing agents are suitable for use in the present invention, although blocked isocyanates are often preferred for cathodic electrodeposition.

[0065] Aminoplast resins, which are often the preferred curing agent for anionic electrodeposition, are the condensation products of amines or amides with aldehydes. Examples of suitable amine or amides are melamine, benzoguanamine, urea and similar compounds. Generally, the aldehyde employed is formaldehyde, although products can be made from other aldehydes, such as acetaldehyde and furfural. The condensation products contain methylol groups or similar alkylol groups depending on the particular aldehyde employed. Often, these methylol groups are etherified by reaction with an alcohol, such as a monohydric alcohol containing from 1 to 4 carbon atoms, such as methanol, ethanol, isopropanol, and n-butanol. Aminoplast resins are commercially available from American Cyanamid Co. under the trademark CYMEL and from Monsanto Chemical Co. under the trademark RESIMENE.

[0066] The aminoplast curing agents are often utilized in conjunction with the active hydrogen containing anionic electrodepositable resin in amounts ranging from 5 percent to 60 percent by weight, such as from 20 percent to 40 percent by weight, the percentages based on the total weight of the resin solids in the electrodepositable composition. As indicated, blocked organic polyisocyanates are often used as the curing agent in cathodic electrodeposition compositions. The polyisocyanates can be fully blocked as described in United States Patent No. 3,984,299 at col. 1, lines 1 to 68, col. 2, and col. 3, lines 1 to 15, or partially blocked and reacted with the polymer backbone as described in United States Patent No. 3,947,338 at col. 2, lines 65 to 68, col. 3, and col. 4 lines 1 to 30, the cited portions of which being incorporated herein by reference. By "blocked" is meant that the isocyanate groups have been reacted with a compound so that the resultant blocked isocyanate group is stable to active hydrogens at ambient temperature but reactive with active hydrogens in the film forming polymer at elevated temperatures usually between 90°C and 200°C.

[0067] Suitable polyisocyanates include aromatic and aliphatic polyisocyanates, including cycloaliphatic polyisocyanates and representative examples include diphenylmethane-4,4'-diisocyanate (MDI), 2,4- or 2,6-toluene diisocyanate (TDI), including mixtures thereof, p-phenylene diisocyanate, tetramethylene and hexamethylene diisocyanates, dicyclohexylmethane-4,4'-diisocyanate, isophorone diisocyanate, mixtures of phenylmethane-4,4'-diisocyanate and polymethylene polyphenylisocyanate. Higher polyisocyanates, such as triisocyanates can be used. An example would include triphenylmethane-4,4',4"-

triisocyanate. Isocyanate ( )-prepolymers with polyols such as neopentyl glycol and trimethylolpropane and with polymeric polyols such as polycaprolactone diols and triols (NCO/OH equivalent ratio greater than 1) can also be used.

[0068] The polyisocyanate curing agents are typically utilized in conjunction with the active hydrogen containing cationic electrodepositable resin in amounts ranging from 5 percent to 60 percent by weight, such as from 20 percent to 50 percent by weight, the percentages based on the total weight of the resin solids of the electrodepositable composition.

[0069] In certain embodiments, the coating composition comprising a film-forming resin also comprises yttrium. In certain embodiments, yttrium is present in such compositions in an amount from 10 to 10,000 ppm, such as not more than 5,000 ppm, and, in some cases, not more than 1,000 ppm, of total yttrium (measured as elemental yttrium). Both soluble and insoluble yttrium compounds may serve as the source of yttrium. Examples of yttrium sources suitable for use in lead-free electrodepositable coating compositions are soluble organic and inorganic yttrium salts such as yttrium acetate, yttrium chloride, yttrium formate, yttrium carbonate, yttrium sulfamate, yttrium lactate and yttrium nitrate. When the yttrium is to be added to an electrocoat bath as an aqueous solution, yttrium nitrate, a readily available yttrium compound, is a preferred yttrium source. Other yttrium compounds suitable for use in electrodepositable compositions are organic and inorganic yttrium compounds such as yttrium oxide, yttrium bromide, yttrium hydroxide, yttrium molybdate, yttrium sulfate, yttrium silicate, and yttrium oxalate. Organoyttrium complexes and yttrium metal can also be used. When the yttrium is to be incorporated into an electrocoat bath as a component in the pigment paste, yttrium oxide is often the preferred source of yttrium.

[0070] The electrodepositable compositions described herein are in the form of an aqueous dispersion. The term "dispersion" is believed to be a two-phase transparent, translucent or opaque resinous system in which the resin is in the dispersed phase and the water is in the continuous phase. The average particle size of the resinous phase is generally less than 1.0 and usually less than 0.5 microns, often less than 0.15 micron.

[0071] The concentration of the resinous phase in the aqueous medium is often at least 1 percent by weight, such as from 2 to 60 percent by weight, based on total weight of the aqueous dispersion. When such compositions are in the form of resin concentrates, they generally have a resin solids content of 20 to 60 percent by weight based on weight of the aqueous dispersion.

[0072] The electrodepositable compositions described herein are often supplied as two components: (1) a clear resin feed, which includes generally the active hydrogen-containing ionic electrodepositable resin, i.e., the main film-forming polymer, the curing agent, and any additional water-dispersible, non-pigmented components; and (2) a pigment paste, which generally includes one or more colorants (described below), a water-dispersible grind resin which can be the same or different from the main-film forming polymer, and, optionally, additives such as wetting or dispersing aids. Electrodeposition bath components (1) and (2) are dispersed in an aqueous medium which comprises water and, usually, coalescing solvents.

[0073] As aforementioned, besides water, the aqueous medium may contain a coalescing solvent. Useful coalescing solvents are often hydrocarbons, alcohols, esters, ethers and ketones. The preferred coalescing solvents are often alcohols, polyols and ketones. Specific coalescing solvents include isopropanol, butanol, 2-ethylhexanol, isophorone, 2-methoxypentanone, ethylene and propylene glycol and the monoethyl monobutyl and monohexyl ethers of ethylene glycol. The amount of coalescing solvent is generally between 0.01 and 25 percent, such as from 0.05 to 5 percent by weight based on total weight of the aqueous medium.

[0074] In addition, a colorant and, if desired, various additives such as surfactants, wetting agents or catalyst can be included in the coating composition comprising a film-forming resin. As used herein, the term "colorant" means any substance that imparts color and/or other opacity and/or other visual effect to the composition. The colorant can be added to the composition in any suitable form, such as discrete particles, dispersions, solutions and/or flakes. A single colorant or a mixture of two or more colorants can be used.

[0075] Example colorants include pigments, dyes and tints, such as those used in the paint industry and/or listed in the Dry Color Manufacturers Association (DCMA), as well as special effect compositions. A colorant may include, for example, a finely divided solid powder that is insoluble but wettable under the conditions of use. A colorant can be organic or inorganic and can be agglomerated or non-agglomerated. Colorants can be incorporated by use of a grind vehicle, such as an acrylic grind vehicle, the use of which will be familiar to one skilled in the art.

[0076] Example pigments and/or pigment compositions include, but are not limited to, carbazole dioxazine crude pigment, azo, monoazo, disazo, naphthol AS, salt type (lakes), benzimidazolone, condensation, metal complex, isoindolinone, isoindoline and polycyclic phthalocyanine, quinacridone, perylene, perinone, diketopyrrolo pyrrole, thioindigo, anthraquinone, indanthrone, anthrapyrimidine, flavanthrone, pyranthrone, anthanthrone, dioxazine, triarylcarbonium, quinophthalone pigments, diketo pyrrolo pyrrole red ("DPPBO red"), titanium dioxide, carbon black and mixtures thereof. The terms "pigment" and "colored filler" can be used interchangeably.

[0077] Example dyes include, but are not limited to, those that are solvent and/or aqueous based such as phthalo green or blue, iron oxide, bismuth vanadate, anthraquinone, perylene, aluminum and quinacridone.

[0078] Example tints include, but are not limited to, pigments dispersed in water-based or water miscible carriers such as AQUA-CHEM 896 commercially available from Degussa, Inc., CHARISMA COLORANTS and MAXITONER INDUSTRIAL COLORANTS commercially available from Accurate Dispersions division of Eastman Chemical, Inc.

[0079] As noted above, the colorant can be in the form of a dispersion including, but not limited to, a nanoparticle dispersion. Nanoparticle dispersions can include one or more highly dispersed nanoparticle colorants and/or colorant particles that produce a desired visible color and/or opacity and/or visual effect. Nanoparticle dispersions can include colorants such as pigments or dyes having a particle size of less than 150 nm, such as less than 70 nm, or less than 30 nm. Nanoparticles can be produced by milling stock organic or inorganic pigments with grinding media having a particle size of less than 0.5 mm. Example nanoparticle dispersions and methods for making them are identified in U.S. Patent No. 6,875,800 B2, which is incorporated herein by reference. Nanoparticle dispersions can also be produced by crystallization, precipitation, gas phase condensation, and chemical attrition (i.e., partial dissolution). In order to minimize re-agglomeration of nanoparticles within the coating, a dispersion of resin-coated nanoparticles can be used. As used herein, a "dispersion of resin-coated nanoparticles" refers to a continuous phase in which is dispersed discreet "composite microparticles" that comprise a nanoparticle and a resin coating on the nanoparticle. Example dispersions of resin-coated nanoparticles and methods for making them are identified in United States Patent Application Publication 2005-

0287348 A1, filed June 24, 2004, U.S. Provisional Application No. 60/482,167 filed June 24, 2003, and United States Patent Application Serial No. 11/337,062, filed January 20, 2006, which is also incorporated herein by reference.

[0080] Example special effect compositions that may be used include pigments and/or compositions that produce one or more appearance effects such as reflectance, pearlescence, metallic sheen, phosphorescence, fluorescence, photochromism, photosensitivity, thermochromism, goniochromism and/or color-change. Additional special effect compositions can provide other perceptible properties, such as opacity or texture. In certain embodiments, special effect compositions can produce a color shift, such that the color of the coating changes when the coating is viewed at different angles. Example color effect compositions are identified in U.S. Patent No. 6,894,086, incorporated herein by reference. Additional color effect compositions can include transparent coated mica and/or synthetic mica, coated silica, coated alumina, a transparent liquid crystal pigment, a liquid crystal coating, and/or any composition wherein interference results from a refractive index differential within the material and not because of the refractive index differential between the surface of the material and the air.

[0081] In certain embodiments, a photosensitive composition and/or photochromic composition, which reversibly alters its color when exposed to one or more light sources, can be used. Photochromic and/or photosensitive compositions can be activated by exposure to radiation of a specified wavelength. When the composition becomes excited, the molecular structure is changed and the altered structure exhibits a new color that is different from the original color of the composition. When the exposure to radiation is removed, the photochromic and/or photosensitive composition can return to a state of rest, in which the original color of the composition returns. In certain embodiments, the photochromic and/or photosensitive composition can be colorless in a non-excited state and exhibit a color in an excited state. Full color-change can appear within milliseconds to several minutes, such as from 20 seconds to 60 seconds. Example photochromic and/or photosensitive compositions include photochromic dyes.

[0082] In certain embodiments, the photosensitive composition and/or photochromic composition can be associated with and/or at least partially bound to, such as by covalent bonding, a polymer and/or polymeric materials of a polymerizable component. In contrast to some coatings in which the photosensitive composition may migrate out of the coating and crystallize into the substrate, the photosensitive composition and/or photochromic composition associated with and/or at least partially bound to a polymer and/or polymerizable component in accordance with certain embodiments of the present invention, have minimal migration out of the coating. Example photosensitive compositions and/or photochromic compositions and methods for making them are identified in U.S. Application Serial No. 10/892,919 filed July 16, 2004, incorporated herein by reference.

[0083] In general, the colorant can be present in the coating composition in any amount sufficient to impart the desired visual and/or color effect. The colorant may comprise from 1 to 65 weight percent, such as from 3 to 40 weight percent or 5 to 35 weight percent, with weight percent based on the total weight of the composition.

[0084] After deposition, the coating is often heated to cure the deposited composition. The heating or curing operation is often carried out at a temperature in the range of from 120 to 250°C, such as from 120 to 190°C, for a period of time ranging from 10 to 60 minutes. In certain embodiments, the thickness of the resultant film is from 10 to 50 microns.

[0085] As will be appreciated by the foregoing description, the present invention is directed to compositions for treating a metal substrate. These compositions comprise: a Group IIIB and/or Group IVB metal; free fluoride; and lithium. The composition, in certain embodiments, is substantially free of heavy metal phosphate, such as zinc phosphate and nickel-containing phosphate, and chromate.

[0086] As has been indicated throughout the foregoing description, the methods and coated substrates of the present invention do not, in certain embodiments, include the deposition of a crystalline phosphate, such as zinc phosphate, or a chromate. As a result, the environmental drawbacks associated with such materials can be avoided. Nevertheless, the methods of the present invention have been shown to provide coated substrates that are, in at least some cases, resistant to corrosion at a level comparable to, in some cases even superior to, methods wherein such materials are used. This is a surprising and unexpected discovery of the present invention and satisfies a long felt need in the art.

[0087] Illustrating the invention are the following examples that are not to be considered as limiting the invention to their details. All parts and percentages in the examples, as well as throughout the specification, are by weight unless otherwise indicated.

EXAMPLE 1

[0088] Twelve cold rolled steel (CRS) panels (panels 1-12) were cleaned by dipping with a solution of Chemkleen 166 M/Chemkleen 171/11, a two component liquid alkaline cleaner available from PPG Industries, for three minutes at 60°C. After alkaline cleaning, the panels were rinsed thoroughly with deionized water and then with deionized water containing 0.25 g/l Zirco Rinse Additive (available commercially from PPG Industries, Quattordio, Italy).

[0089] Six of these panels (panels 1-6) were immersed in a zirconium pretreatment solution for two minutes at ambient temperature, designated in Tables 2 and 3 as "Pretreatment A." Pretreatment A was prepared by diluting 4.5 liters Zircobond ZC (a hexafluorozirconic acid copper containing agent available commercially from PPG Industries, Quattordio, Italy) with approximately 400 liters of deionized water to a zirconium concentration of 175 ppm (as zirconium) and adjusting the pH to 4.5 with Chemfill Buffer/M (a mild alkaline buffering agent available commercially from PPG Industries, Quattordio, Italy).

[0090] After pretreatment in a solution of Pretreatment A, panels 1-6 were rinsed with deionized water containing 0.25 g/l Zirco Rinse Additive, then were thoroughly rinsed with deionized water, and then were dried for 10 minutes in an oven at 70°C. Panels 1-6 had a light bronze appearance and the coating thickness was measured using a portable X-ray Fluorescence instrument (XRF) at approximately 39 nm.

[0091] The pretreatment solution referred to in Table 2 as "Pretreatment B" was prepared by adding 1 g/l lithium nitrate (available from Sigma Aldrich code 227986) to Pretreatment A solution in order to obtain a concentration of 100 ppm lithium. Each panel was dried by placing it in an oven at 70°C for approximately ten minutes. The coating thickness as measured by XRF was approximately 39 nm.

[0092] All of the panels that were pretreated with either Pretreatment A or Pretreatment B were subsequently coated with G6MC2, a yttrium-containing cathodic electrocoat commercially available from PPG Industries that contains 422 g of resin (W7827, commercially available from PPG Industries, Inc.), 98 g of paste (P9757, commercially available from PPG Industries, Inc.), and 480 g of water. The G6MC3 coating bath was prepared and coated according to the manufacturer's instructions. The panels were cured according to the manufacturer's specifications.

[0093] After curing, three of the coated panels pretreated with Pretreatment A and three of the coated panels pretreated with Pretreatment B were subjected to a VW cyclic corrosion test PV1210. After a scribe and a first stone chipping, the three coated panels pretreated with Pretreatment A and the three panels pretreated with Pretreatment B were exposed to condensing humidity (4 hours NSS at 35°C then 4 hours at 23°C and 50% humidity followed by 16 hours at 40°C and 100% humidity) for 30 days, and then a second VW cyclic corrosion PV1210 test was run on the exposed panels. The stone chipping results were rated on a scale of 0 to 5, where 5 indicates complete paint loss, and 0 indicates perfect paint adhesion. After humidity exposure, the corrosion creepage along the scribe and stone chipping results were measured.

[0094] The remaining three coated panels pretreated with Pretreatment A and the remaining three coated panels pretreated with Pretreatment B were subjected to a GM cyclic corrosion test in which the panels were scratched by cutting through the coating system down to metal. The panels were exposed to condensing humidity (8 hours at 25°C and 45% humidity then 8 hours at 49°C and 100% humidity followed by 8 hours at 60°C and 30% humidity) for 40 days. At the end of the test, the panels were rated by measuring the paint loss from the scribe (creep) and the maximum creepage (both sides) calculated in millimeters for each panel. Results are summarized in Table 2 below.

[0095] The film on the panels pretreated with Pretreatment B were tested using Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS), which indicated that the film consists of zirconium, oxygen, fluoride, and lithium. Lithium was present throughout the film.

Table 2

Pretreatment	Electrocoat	28 cycles GMW 14872 test	30 cycles VW PV1210 test	
		Corrosion along the scribe (mm)	Corrosion along the scribe (mm)	Stone chipping creepage rating[
A	G6MC3	9.5	1.2	4.0
B	G6MC3	6.3	0.8	3.0

EXAMPLE 2

[0096] Cold rolled steel panels were pretreated as in Example 1, with half of the panels being pretreated with Pretreatment A and the other half being pretreated with "Pretreatment C," where Pretreatment C was prepared by adding lithium nitrate and sodium molybdenum to Pretreatment A in order to obtain a concentration of 40 ppm molybdenum and 100 ppm lithium. Each panel was dried by placing it in an oven at 70°C for approximately ten minutes. The coating thickness as measured by XRF was approximately 40 nm.

[0097] The panels were subsequently electrocoated with ED 6070/2, a yttrium-containing cathodic electrocoat commercially available from PPG Industries that contains 472 g of resin (W7910, commercially available from PPG Industries, Inc.), 80 g of paste (P9711, commercially available from PPG Industries, Inc.), and 448 g of water. The panels were subjected to the VW cyclic corrosion test PV1210. The results appear in Table 3 below.

[0098] The film on the panels pretreated with Pretreatment C was tested using ToF-SIMS, X-Ray Photoelectron Spectroscopy (XPS), and X-Ray Fluorescence Spectroscopy (XRF). ToF-SIMS indicated the presence of lithium and molybdenum throughout the coating and that molybdenum was present in the mixed oxide form. XPS and XRF confirmed the presence of molybdenum at 1-10% of the zirconium oxide film weight. Zirconium, oxygen, fluoride, lithium, and molybdenum were present in the film.

Table 3

Pretreatment	Electrocoat	30 cycles VW PV1210 test	
		Corrosion along the scribe (mm)	Stone chipping creepage rating
A	ED6070/2	0.75	2.5
C	ED6070/2	0.5	2

[0099] It will be appreciated by those skilled in the art that changes could be made to the embodiments described above without departing from the broad inventive concept thereof. It is understood, therefore, that this invention is not limited to the particular embodiments disclosed, but it is intended to cover modifications which are within the spirit and scope of the invention, as defined by the appended claims.

WHAT IS CLAIMED IS:

1. A pretreatment composition for treating a metal substrate comprising:
a Group IIIB and/or Group IVB metal;
free fluoride; and
lithium.

2. The pretreatment composition of claim 1, wherein the pretreatment composition comprises a Group IVB metal.

3. The pretreatment composition of claim 2, wherein the Group IVB metal is provided in the form of hexafluorozirconic acid, hexafluorotitanic acid, or salts thereof.

4. The pretreatment composition of claim 2, wherein the Group IVB metal is zirconium.

5. The method according to claim 1, wherein the Group IVB metal is provided in the form of oxides or hydroxides of zirconium.

6. The method according to claim 1, wherein the Group IVB metal is provided in the form of zirconyl nitrate, zirconyl sulfate, or zirconium basic carbonate.

7. The pretreatment composition of claim 1, wherein the Group IIIB and/or Group IVB metal is provided in the form of an acid or salt.

8. The pretreatment composition of claim 1, wherein the Group IIIB and/or Group IVB metal comprises from 50 to 500 parts per million metal, based on a total weight of the ingredients in the pretreatment composition.

9. The pretreatment composition of claim 1, wherein the Group IIIB and/or Group IVB metal comprises from 75 to 250 parts per million metal, based on a total weight of the ingredients in the pretreatment composition.

10. The pretreatment composition of claim 1, wherein a molar ratio of the Group IIIB and/or Group IVB metal to the lithium is between 100: 1 and 1:10.

11. The pretreatment composition of claim 1, wherein the free fluoride comprises from 5 to 250 ppm of the pretreatment composition.

12. The method according to claim 1, wherein the free fluoride comprises from 25 to 200 ppm of the pretreatment composition.

13. The pretreatment composition of claim 1, wherein the lithium is provided in the form of a salt.

14. The pretreatment composition of claim 1, wherein the salt is lithium nitrate, lithium sulfate, lithium fluoride, lithium chloride, lithium hydroxide, lithium carbonate, or lithium iodide.

15. The pretreatment composition of claim 1, wherein the lithium comprises from 5 to 500 parts per million, based on a total weight of the ingredients in the pretreatment composition.

16. The pretreatment composition of claim 1, wherein the lithium comprises less than 200 parts per million, based on a total weight of the ingredients in the pretreatment composition.

17. The pretreatment composition of claim 1, wherein the lithium comprises from 25 to 125 parts per million, based on a total weight of the ingredients in the pretreatment composition.

18. The pretreatment composition of claim 1, wherein the pretreatment composition is substantially free of phosphate ions.

19. The pretreatment composition of claim 1, wherein the pretreatment composition is substantially free of chromate.

20. The pretreatment composition of claim 1, wherein the pretreatment composition is aqueous.

21. The pretreatment composition of claim 1, wherein the pretreatment composition is used in a dip application.

22. The pretreatment composition of claim 1, wherein the pretreatment composition is used in a spray application.

23. The pretreatment composition of claim 1, wherein a K ratio is equal to A/B, wherein A is a mole weight of a compound (A) containing the Group IIIB and/or Group IVB metal, and wherein B is a mole weight calculated as HF of a compound containing fluorine as a supplying source of the fluoride, wherein $K>0.10$.

24. The pretreatment composition of claim 1, wherein a K ratio is equal to A/B, wherein A is a mole weight of a compound (A) containing the Group IIIB and/or Group IVB metal, and wherein B is a mole weight calculated as HF of a compound containing fluorine as a supplying source of the fluoride, wherein $0.11<K<0.25$.

25. The pretreatment composition of claim 1, further comprising an electropositive metal.

26. The pretreatment composition of claim 25, wherein the electropositive metal is selected from the Group consisting of copper, nickel, silver, gold, and combinations thereof.

27. The pretreatment composition of claim 25, wherein the electropositive metal comprises copper.

28. The pretreatment composition of claim 27, wherein the copper is provided in the form of copper nitrate, copper sulfate, copper chloride, copper carbonate, or copper fluoride.

29. The pretreatment composition of claim 25, wherein the electropositive metal comprises from 0 to 100 parts per million, based on a total weight of the ingredients in the pretreatment composition.

30. The pretreatment composition of claim 25, wherein the electropositive metal comprises from 2 to 35 parts per million, based on a total weight of the ingredients in the pretreatment composition.

31. The pretreatment composition of claim 1, further comprising molybdenum.

32. The pretreatment composition of claim 31, wherein the molybdenum is provided in the form of a salt.

33. The pretreatment composition of claim 32, wherein the salt is sodium molybdate, calcium molybdate, potassium molybdate, ammonium molybdate, molybdenum chloride, molybdenum acetate, molybdenum sulfamate, molybdenum formate, or molybdenum lactate.

34. The pretreatment composition of claim 31, wherein the molybdenum comprises from 5 to 500 parts per million, based on a total weight of the ingredients in the pretreatment composition.

35. The pretreatment composition of claim 31, wherein the molybdenum comprises from 5 to 150 parts per million, based on a total weight of the ingredients in the pretreatment composition.

36. A method for treating a metal substrate comprising contacting the metal substrate with a pretreatment composition comprising a Group IIIB and/or Group IVB metal, free fluoride, and lithium.

37. The method according to claim 36, wherein the pretreatment composition further comprises molybdenum.

38. The method according to claim 36, further comprising electrophoretically depositing a coating composition onto the metal substrate.

39. The method according to claim 38, wherein the coating composition comprises yttrium.

40. A method of coating a metal substrate comprising electrophoretically depositing a coating composition onto the metal substrate, wherein the metal substrate comprises a treated surface layer comprising a Group IIIB and/or Group IVB metal, fluoride, and lithium.

41. A pretreated metal substrate comprising a surface layer comprising a Group IIIB and/or IVB metal, free fluoride, and lithium on at least a portion of the substrate.

42. An electrophoretically coated metal substrate comprising:

a treated surface layer comprising a Group IIIB and/or Group IVB metal, fluoride, and lithium on a surface of the metal substrate; and

an electrophoretically deposited coating over at least a portion of the treated surface layer.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2013/055350

A. CLASSIFICATION OF SUBJECT MATTER
INV. C23C22/34 C25D13/20 C23C22/44 C23C22/83
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C23C C25D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2008/008902 A1 (TAKAKUWA HIDEKI [JP] ET AL) 10 January 2008 (2008-01-10)	1,2,4-9, 11,12, 14, 18-23, 36,38, 40-42
Y	page 1, paragraph 16 - page 5, paragraph 106 examples 2, 3 page 7, paragraph 133 - page 8, paragraph 173 examples 2,3; tables 1-5 claims 1-4 ----- -/--	39

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search 6 November 2013	Date of mailing of the international search report 13/11/2013
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Handrea-Haller, M

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INTERNATIONAL SEARCH REPORT

International application No
PCT/US2013/055350

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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INTERNATIONAL SEARCH REPORT

International application No
PCT/US2013/055350

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2006/043727 A1 (NIHON PARKERIZING [JP]; OSHITA KENICHIRO [JP]; TANAKA MUNENORI [JP]) 27 April 2006 (2006-04-27) page 49; examples 306,320; table 13 -----	1,2,7, 10,15, 16, 18-21, 31,36, 37,41
Y	US 2008/145678 A1 (MCMURDIE NEIL D [US] ET AL) 19 June 2008 (2008-06-19) examples 1-3 -----	39

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Form PCT/ISA/210 (continuation of second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2013/055350

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C23C 22/44(2006.01)
C23C 22/83(2006.01)

权利要求书2页 说明书14页

(54) 发明名称

含锂的锆预处理组合物，处理金属基材的相关方法，和相关的经涂覆的金属基材

(57) 摘要

公开了预处理组合物和用预处理组合物处理金属基材的相关方法，包所述金属基材括含铁基材，例如冷轧钢和电镀锌钢。所述预处理组合物包括：第 IIIB 族和／或第 IVB 族金属；游离氟离子；和锂。所述方法包括将所述金属基材与所述预处理组合物接触。

1. 用于处理金属基材的预处理组合物，包含：

第 IIIB 族和 / 或第 IVB 族金属；

游离氟离子；和

锂。

2. 权利要求 1 所述的预处理组合物，其中所述预处理组合物包含第 IVB 族金属。

3. 权利要求 2 所述的预处理组合物，其中所述第 IVB 族金属以六氟锆酸、六氟钛酸、或其盐的形式提供。

4. 权利要求 2 所述的预处理组合物，其中所述第 IVB 族金属是锆。

5. 根据权利要求 1 所述的方法，其中所述第 IVB 族金属以锆的氧化物或氢氧化物的形式提供。

6. 根据权利要求 1 所述的方法，其中所述第 IVB 族金属以硝酸氧锆、硫酸氧锆、或碱式碳酸锆的形式提供。

7. 权利要求 1 所述的预处理组合物，其中所述第 IIIB 族和 / 或第 IVB 族金属以酸或盐的形式提供。

8. 权利要求 1 所述的预处理组合物，其中所述第 IIIB 族和 / 或第 IVB 族金属基于所述预处理组合物中成分的总重量计为每百万份金属 50-500 份。

9. 权利要求 1 所述的预处理组合物，其中所述第 IIIB 族和 / 或第 IVB 族金属基于所述预处理组合物中成分的总重量计为每百万份金属 75-250 份。

10. 权利要求 1 所述的预处理组合物，其中第 IIIB 族和 / 或第 IVB 族金属与锂的摩尔比为 100：1-1：10。

11. 权利要求 1 所述的预处理组合物，其中所述游离氟离子占所述预处理组合物的 5-250ppm。

12. 根据权利要求 1 所述的方法，其中所述游离氟离子占所述预处理组合物的 25-200ppm。

13. 权利要求 1 所述的预处理组合物，其中所述锂以盐的形式提供。

14. 权利要求 1 所述的预处理组合物，其中所述盐是硝酸锂、硫酸锂、氟化锂、氯化锂、氢氧化锂、碳酸锂、或碘化锂。

15. 权利要求 1 所述的预处理组合物，其中所述锂基于所述预处理组合物中的成分的总重量计为 5-500 百万分率。

16. 权利要求 1 所述的预处理组合物，其中所述锂基于所述预处理组合物中的成分的总重量计为少于 200 百万分率。

17. 权利要求 1 所述的预处理组合物，其中所述锂基于所述预处理组合物中的成分的总重量计为 25-125 百万分率。

18. 权利要求 1 所述的预处理组合物，其中所述预处理组合物基本上不含磷酸根离子。

19. 权利要求 1 所述的预处理组合物，其中所述预处理组合物基本上不含铬酸盐。

20. 权利要求 1 所述的预处理组合物，其中所述预处理组合物是含水的。

21. 权利要求 1 所述的预处理组合物，其中所述预处理组合物在浸涂中使用。

22. 权利要求 1 所述的预处理组合物，其中所述预处理组合物在喷涂中使用。

23. 权利要求 1 所述的预处理组合物，其中 K 比率等于 A/B，其中 A 是含第 IIIB 族和 /

或第 IVB 族金属的化合物 (A) 的摩尔重量，以及其中 B 是作为 HF 计算的含氟化合物的摩尔重量，所述含氟化合物作为氟离子的供应源，其中 K>0.10。

24. 权利要求 1 所述的预处理组合物，其中 K 比率等于 A/B，其中 A 是含第 IIIB 族和 / 或第 IVB 族金属的化合物 (A) 的摩尔重量，以及其中 B 是作为 HF 计算的含氟化合物的摩尔重量，所述含氟化合物作为氟离子的供应源，其中 0.11<K<0.25。

25. 权利要求 1 所述的预处理组合物，进一步包含正电性金属。

26. 权利要求 25 所述的预处理组合物，其中所述正电性金属选自铜、镍、银、金、及其组合。

27. 权利要求 25 所述的预处理组合物，其中所述正电性金属包括铜。

28. 权利要求 27 所述的预处理组合物，其中所述铜以硝酸铜、硫酸铜、氯化铜、碳酸铜、或氟化铜的形式提供。

29. 权利要求 25 所述的预处理组合物，其中所述正电性金属基于所述预处理组合物中的成分的总重量计为 0-100 百万分率。

30. 权利要求 25 所述的预处理组合物，其中所述正电性金属基于所述预处理组合物中的成分的总重量计为 2-35 百万分率。

31. 权利要求 1 所述的预处理组合物，进一步包含钼。

32. 权利要求 31 所述的预处理组合物，其中所述钼以盐的形式提供。

33. 权利要求 32 所述的预处理组合物，其中所述盐是钼酸钠、钼酸钙、钼酸钾、钼酸铵、氯化钼、乙酸钼、氨基磺酸钼、甲酸钼、或乳酸钼。

34. 权利要求 31 所述的预处理组合物，其中所述钼基于所述预处理组合物中的成分的总重量计为 5-500 百万分率。

35. 权利要求 31 所述的预处理组合物，其中所述钼基于所述预处理组合物中的成分的总重量计为 5-150 百万分率。

36. 处理金属基材的方法，包括将所述金属基材与包含第 IIIB 族和 / 或第 IVB 族金属、游离氟离子、和锂的预处理组合物接触。

37. 根据权利要求 36 所述的方法，其中所述预处理组合物进一步包含钼。

38. 根据权利要求 36 所述的方法，进一步包括将涂料组合物电泳沉积到所述金属基材之上。

39. 根据权利要求 38 所述的方法，其中所述涂料组合物包含钇。

40. 涂覆金属基材的方法，包括将涂料组合物电泳沉积到所述金属基材之上，其中所述金属基材包括含第 IIIB 族和 / 或第 IVB 族金属、氟离子、和锂的经处理的表面层。

41. 经预处理的金属基材，其在至少一部分基材上包括含第 IIIB 族和 / 或第 IVB 族金属、游离氟离子、和锂的表面层。

42. 经电泳涂覆的金属基材，包括：

经处理的表面层，其在所述金属基材的表面上包含第 IIIB 族和 / 或第 IVB 族金属、氟离子、和锂；和

在至少一部分所述经处理的表面层上的经电泳沉积的涂层。

含锂的锆预处理组合物，处理金属基材的相关方法，和相关的经涂覆的金属基材

发明领域

[0001] 本发明涉及预处理组合物和处理金属基材（包括含铁基材例如冷轧钢和电镀锌钢，或铝合金）的方法。本发明还涉及经涂覆的金属基材。

[0002] 发明背景

[0003] 将保护涂层用于金属基材以改进耐腐蚀性和涂料附着性是常见的。涂覆这种基材的常规的技术包括涉及用磷酸盐转化涂料和含铬冲洗预处理所述金属基材。然而，这种含磷酸盐和／或铬酸盐的组合物的使用，带来了环境和健康的忧虑。

[0004] 因此，已经开发了不含铬酸盐和／或不含磷酸盐的预处理组合物。这种组合物通常基于化学混合物，所述化学混合物与基材表面反应并粘结到其之上以形成保护层。例如，基于第 IIIB 族或第 IVB 族金属化合物的预处理组合物最近变得更加流行。这种组合物经常含有游离氟的源，即与预处理组合物分离的氟，而不是与另一种元素（例如第 IIIB 族或 IVB 族金属）键连的氟。游离氟可蚀刻金属基材的表面，由此促进第 IIIB 族或第 IVB 族金属涂料的沉积。然而，这些预处理组合物的耐腐蚀性能力通常显著地弱于常规的磷酸盐和／或含铬的预处理。

[0005] 期望提供克服至少一些之前描述的现有技术的缺点（包括与铬酸盐和／或磷酸盐的使用相关的环境缺点）的用于处理金属基材的方法。还期望提供处理金属基材的方法，所述方法将赋予等于，或甚至优于通过使用磷酸盐转化涂料赋予的耐腐蚀性能的耐腐蚀性能。还期望提供相关的经涂覆的金属基材。

[0006] 发明概述

[0007] 在某些方面，本发明涉及用于处理金属基材的预处理组合物，所述预处理组合物包括：第 IIIB 族和／或第 IVB 族金属；游离氟离子；和锂。

[0008] 在仍其它方面，本发明涉及处理金属基材的方法，包括将所述金属基材与包含第 IIIB 族和／或第 IVB 族金属、游离氟离子、和锂的预处理组合物接触。

[0009] 在仍其它方面，本发明涉及涂覆金属基材的方法，包括将涂料组合物电泳沉积到所述金属基材之上，其中所述金属基材包含经处理的表面层，其包含第 IIIB 族和／或第 IVB 族金属、游离氟离子、和锂。

[0010] 在仍其它方面，本发明涉及包括表面层的经预处理的金属基材，所述表面层在所述基材的至少一部分上包含第 IVB 族金属、游离氟离子、和锂。

[0011] 在仍其它方面，本发明涉及经电泳涂覆的金属基材，包括：经处理的表面层，其在所述金属基材的表面上包含第 IIIB 族和／或第 IVB 族金属、游离氟离子、和锂；和在经处理的表面层的至少一部分之上的经电泳沉积的涂层。

[0012] 详细说明

[0013] 为了以下详细说明的目的，除了在有明确相反的说明的情况之外，应理解可假设各种备选的变化形式和步骤顺序。此外，除了在任何操作实施例中，或其中另有说明，否则用于表达在说明书和权利要求中成分的用量的全部数值应理解为在所有情况下被术语

“约”修饰。因此，除非有相反的说明，否则在下面的说明书和所附权利要求中给出的数值参数是取决于本发明所获得的期望性能来变化的约数。最起码，并且不试图限制对权利要求的范围适用等同原则，各数值参数应该至少按照报道的有效数字的数值并采用普通的舍入技术来解释。

[0014] 尽管阐明本发明的宽范围的数值范围和参数是约数，但是在具体实施例中所述的数值是尽量精确报道的。然而，任何数值固有地含有必然地从在它们各自试验测量中存在的标准偏差获得的必然的误差。

[0015] 同样地，应理解本文所记载的任何数值范围都意图包含含在其中的所有子范围。例如，范围“1 至 10”意图包括所记载的最小值 1 和所记载的最大值 10 之间（并且包括 1 和 10）的所有子范围，即，具有等于或者大于 1 的最小值和等于或者小于 10 的最大值。

[0016] 在本申请中，除非另有具体说明，否则单数的使用包括复数并且复数涵盖单数。此外，在本申请中，除非另有具体说明，“或”的使用是指“和／或”，但是“和／或”在某些情况下可以是明确使用的。

[0017] 除非本文另有公开，本文使用的术语“基本上不含”是指特定的材料不是有意地将添加到组合物中并且仅以痕量或作为杂质存在。本文使用的术语″完全不含″是指组合物不包含特定的材料。即，所述组合物包含 0 重量%的这种材料。

[0018] 预处理组合物的某些实施方式涉及用于处理金属基材的预处理组合物，所述金属基材包含第 IIIB 族和／或第 IVB 族金属、游离氟离子、和锂。在某些实施方式中，预处理组合物可基本上不含磷酸盐和／或铬酸盐。与没有用经预处理的组合物（无需磷酸盐或铬酸盐）预处理的基材相比，用所述预处理组合物处理所述金属基材导致基材的改进的耐腐蚀性。在预处理组合物中加入锂和／或锂与钼的结合可提供钢和钢基材的改进的腐蚀性能。

[0019] 本发明的某些实施方式涉及组合物和处理金属基材的方法。用于本发明的合适的金属基材包括经常用于汽车车身、汽车部件、和其它制品，例如小金属部件，包括扣件，即，螺帽、螺栓、螺丝钉、大头针、圆钉、回形针、按钮等的装配中的那些。合适的金属基材的具体的例子包括但不限于，冷轧钢，热轧钢，由锌金属、锌化合物、或锌合金涂覆的钢，例如电镀锌钢，热浸镀锌钢，合金化热浸钢，和镀有锌合金的钢。还可以使用铝合金，镀有铝的钢和镀由铝合金的钢基材。其它合适的有色金属包括铜和镁，以及这些材料的合金。此外，由本发明方法处理的金属基材可以是以其它方式处理和／或涂覆于其剩余表面的基材的切边。根据本发明方法处理的金属基材可以是，例如，金属板或预制件的形式。

[0020] 根据本发明方法待处理的基材可首先被清洁以除去油脂、污物、或其它外来杂质。这可以通过采用温和或强碱性清洁剂（例如可商购以及常规地用于金属预处理工艺中）来完成。用于本发明的碱性清洁剂的合适的例子包括各自商购自 PPG Industries 的 Chemkleen 163、Chemkleen 166M/C、Chemkleen 490MX、Chemkleen 2010LP、Chemkleen166HP、Chemkleen 166M、Chemkleen 166M/Chemkleen 171/11，Inc。经常在水冲洗之前和／或之后，使用这种清洁剂。

[0021] 在某些实施方式中，在预处理步骤之前，基材可以与预冲洗的溶液接触。预冲洗溶液通常可使用某些可溶性金属离子或其它无机材料（例如磷酸盐或简单或复杂的氟化物或酸）以增强经预处理的金属基材的腐蚀保护。可用于本发明的合适的非铬预冲洗溶液公开在美国专利申请号 2010/0159258A1 中，转让给 PPG Industries，Inc，并通过引用并入本

文。

[0022] 本发明的某些实施方式涉及处理金属基材的方法（有或无任选的预冲洗），所述方法包括将所述金属基材与包含第 IIIB 族和 / 或第 IVB 族金属的预处理组合物接触。本文使用的术语“预处理组合物”是指这样的组合物，其在接触基材之后，与所述基材表面反应并化学地改变所述基材表面并粘结于其之上以形成保护涂层。

[0023] 预处理组合物可包含经常是水介质的载体以使得所述组合物是在载体中的第 IIIB 族或第 IVB 族金属化合物的溶液或分散体的形式。在这些实施方式中，可通过任何各种已知的技术（例如浸涂(dipping)或浸渍涂覆(immersion)、喷涂、间歇喷涂、浸涂过后是喷涂、喷涂过后是浸涂、刷涂、或辊涂）使溶液或分散体与基材接触。在某些实施方式中，当施涂于金属基材上时，溶液或分散体处于范围为 60-185° F(15-85℃）的温度。例如，预处理工艺可在环境或室温下进行。接触时间经常为 10 秒 -5 分钟，例如 30 秒 -2 分钟。

[0024] 本文使用的术语“第 IIIB 族和 / 或第 IVB 族金属”是指在 CAS 元素周期表的第 IIIB 族或第 IVB 族中的元素。在适用的情况下，可以使用金属本身。在某些实施方式中，使用第 IIIB 族和 / 或第 IVB 族金属化合物。本文使用的术语“第 IIIB 族和 / 或第 IVB 族金属化合物”是指包括在 CAS 元素周期表第 IIIB 族或第 IVB 族中的至少一种元素的化合物。

[0025] 在某些实施方式中，预处理组合物中使用的第 IIIB 族和 / 或第 IVB 族金属化合物是锆、钛、铪、钇、铈的化合物，或其混合物。锆的合适的化合物包括但不限于，六氟锆酸、碱金属及其铵盐、碳酸锆铵、硝酸氧锆、硫酸氧锆、羧酸锆和羟基羧酸锆，例如氢氟锆酸、乙酸锆、草酸锆、乙醇酸锆铵、乳酸锆铵、柠檬酸锆铵、及其混合物。钛的合适的化合物包括但不限于，氟钛酸及其盐。铪的合适的化合物包括但不限于，硝酸铪。钇的合适的化合物包括但不限于，硝酸钇。铈的合适的化合物包括但不限于，硝酸铈。

[0026] 在某些实施方式中，第 IIIB 族和 / 或第 IVB 族金属基于所述预处理组合物的所有成分的总重量计以 50-500 百万分率（“ppm”）（例如 75-250ppm）金属的量存在于所述预处理组合物中。所述预处理组合物中第 IIIB 族和 / 或第 IVB 族金属的量的范围可在所引述值之间并且包括所引述值。

[0027] 预处理组合物还包含游离氟离子。本发明预处理组合物中的游离氟离子的源可变化。例如，在某些情况下，游离氟离子可得自用于预处理组合物中的第 IIIB 族和 / 或第 IVB 族金属化合物，例如，六氟锆酸就是这种情况。随着第 IIIB 族和 / 或第 IVB 族金属在预处理工艺期间沉积在金属基材之上，六氟锆酸中的氟将变成游离氟离子并且预处理组合物中的游离氟离子的水平（如果任其发展）将随着时间而增长，这是由于用本发明预处理组合物预处理了金属。

[0028] 此外，本发明预处理组合物中的游离氟离子的源可包括除了第 IIIB 族和 / 或第 IVB 族金属化合物之外的化合物。这种源的非限制性的例子包括 HF、NH_4F、NH_4HF_2、NaF、和 $NaHF_2$。本文使用的术语“游离氟离子”是指分离的氟离子。在某些实施方式中，游离氟离子基于所述预处理组合物中的成分的总重量计以 5-250ppm，例如 25-100ppm 的量存在于所述预处理组合物中。所述预处理组合物中的游离氟离子的量的范围可在所引述值之间并且包括所引述值。

[0029] 在某些实施方式中，以摩尔重量计的含第 IIIB 族和 / 或第 IVB 族金属的化合物(A)与以摩尔重量计的作为 HF 计算的含氟化合物(B)（作为游离氟离子的供应源）的 K 比

率具有 $K = A/B$ 的比率，其中 $K>0.10$。在某些实施方式中，$0.11<K<0.25$。

[0030] 预处理组合物还包含锂。在某些实施方式中，用于预处理组合物中的锂的源是盐的形式。合适的锂盐是硝酸锂、硫酸锂、氟化锂、氯化锂、氢氧化锂、碳酸锂、和碘化锂。在某些实施方式中，在预处理组合物中加入锂导致钢和钢基材的改进的耐腐蚀性。

[0031] 在某些实施方式中，锂基于所述预处理组合物中的成分的总重量计以 5-500ppm，例如 25-125ppm 的量存在于所述预处理组合物中。在某些实施方式中，锂以少于 200ppm 的量存在于所述预处理组合物中。所述预处理组合物中的锂的量的范围可在所引述值之间并且包括所引述值。

[0032] 在某些实施方式中，第 IIIB 族和/或第 IVB 族金属与锂的摩尔比为 100:1-1:100，例如，12:1-1:50。

[0033] 在某些实施方式中，预处理组合物还包含正电性金属。本文使用的术语“正电性金属”是指比金属基材的正电性更强的金属。这是指，为了本发明的目的，术语“正电性金属”涵盖比所处理的金属基材的金属更不容易氧化的金属。如本领域技术人员所领会的，金属被氧化的趋势被称作氧化电位，以伏特来表述，以及相对于标准氢电极（其被专门赋予零的氧化电位）来测量。多种元素的氧化电位在下表 1 中列出。如果一种元素具有比所对比的元素更高的电压值（E*，在下表中），则一种元素比另一种元素更不容易被氧化。

[0034] 表 1

[0035]

元素	半电池反应	电压，E*
钾	$K^{+}+e \rightarrow K$	-2.93
钙	$Ca^{2+}+2e \rightarrow Ca$	-2.87

[0036]

元素	半电池反应	电压，E*
钠	$Na^{+}+e \rightarrow Na$	-2.71
镁	$Mg^{2+}+2e \rightarrow Mg$	-2.37
铝	$Al^{3+}+3e \rightarrow Al$	-1.66
锌	$Zn^{2+}+2e \rightarrow Zn$	-0.76
铁	$Fe^{2+}+2e \rightarrow Fe$	-0.44
镍	$Ni^{2+}+2e \rightarrow Ni$	-0.25
锡	$Sn^{2+}+2e \rightarrow Sn$	-0.14
铅	$Pb^{2+}+2e \rightarrow Pb$	-0.13
氢	$2H^{+}+2e \rightarrow H_2$	-0.00

铜	$Cu^{2+}+2e \rightarrow Cu$	0.34
汞	$Hg_2^{2+}+2e \rightarrow 2Hg$	0.79
银	$Ag^{+}+e \rightarrow Ag$	0.80
金	$Au^{3+}+3e \rightarrow Au$	1.50

[0037] 因此，如将清楚地表明，当金属基材包含较早列出的材料中的一种时，例如冷轧钢，热轧钢，由锌金属、锌化合物、或锌合金涂覆的钢，电镀锌钢，热浸镀锌钢，合金化热浸钢，和镀有锌合金、铝合金的钢，镀有铝的钢，镀有铝合金的钢，镁和镁合金，在其上沉积的合适的正电性金属包括，例如，镍、铜、银、和金、以及其混合物。

[0038] 在其中正电性金属包括铜的某些实施方式中，可溶和不可溶的化合物均可充当预处理组合物中的铜的源。例如，预处理组合物中铜离子的供应源可以是水可溶性铜化合物。这种材料的具体的例子包括但不限于，氰化铜、亚铜氰化钾、硫酸铜、硝酸铜、焦磷酸铜、硫氰酸亚铜、乙二胺四乙酸二钠铜四水合物、溴化铜、氧化铜、氢氧化铜、氯化铜、氟化铜、葡萄酸铜、柠檬酸铜、月桂酰肌氨酸铜、甲酸铜、乙酸铜、丙酸铜、丁酸铜、乳酸铜、草酸铜、植酸铜、酒石酸铜、苹果酸铜、琥珀酸铜、丙二酸铜、马来酸铜、苯甲酸铜、水杨酸铜、天门冬氨酸铜、谷氨酸铜、富马酸铜、甘油磷酸铜、叶绿素铜钠、氟硅酸铜、氟硼酸铜和碘酸铜、以及羧酸（从甲酸到癸酸的同系物）的铜盐、多元酸（从草酸到辛二酸的同系物）的铜盐、和羟基羧酸（包括乙醇酸、乳酸、酒石酸，苹果酸和柠檬酸）的铜盐。

[0039] 当由这种水可溶性铜化合物提供的铜离子以硫酸铜，氧化铜等的形式作为杂质沉淀，可期望添加抑制铜离子沉淀的络合剂，由此将它们稳定成溶液中的铜络合物。

[0040] 在某些实施方式中，将铜化合物作为铜络盐例如 $K_3Cu(CN)_4$ 或 Cu-EDTA 加入，所述铜络盐可以以其本身在预处理组合物中稳定存在，但也可能形成铜络合物，其通过将络合剂与以其本身难以溶解的化合物结合可以在预处理组合物中稳定存在。它们的例子包括通过 CuCN 与 KCN 的结合或 CuSCN 与 KSCN 或 KCN 的结合形成的氰化铜络合物，和通过 $CuSO_4$ 和 EDTA·2Na 的结合形成的 Cu-EDTA 络合物。

[0041] 关于络合剂，可以使用可与铜离子形成络合物的化合物；它们的例子包括无机化合物例如氰化物化合物和硫氰酸盐化合物，和多羧酸，并且它们的具体的例子包括乙二胺四乙酸，乙二胺四乙酸的盐例如乙二胺四乙酸二氢二钠二水合物，氨基羧酸例如氨三乙酸和亚氨基二乙酸，羟基羧酸例如柠檬酸和酒石酸、琥珀酸、草酸、乙二胺四亚甲基膦酸、和甘氨酸。

[0042] 在某些实施方式中，正电性金属基于所述预处理组合物的所有成分的总重量计以少于 100ppm，例如 1 或 2ppm-35 或 40ppm 的量存在于所述预处理组合物中。所述预处理组合物中的正电性金属的量的范围可在所引述值之间并且包括所引述值。

[0043] 在某些实施方式中，预处理组合物还可包含钼。在某些实施方式中，所述预处理组合物中使用的钼的源是盐的形式。合适的钼盐是钼酸钠、钼酸钙、钼酸钾、钼酸铵、氯化钼、乙酸钼、氨基磺酸钼、甲酸钼、或乳酸钼。

[0044] 在某些实施方式中，钼基于所述预处理组合物中的成分的总重量计以 5-500ppm，

例如5-150ppm的量存在于所述预处理组合物中。所述预处理组合物中钼的量的范围可在所引述值之间并且包括所引述值。

[0045] 在某些实施方式中，预处理组合物的pH的范围为1-6，例如2-5.5。根据需要可使用，例如，任何酸或碱来调节预处理组合物的pH。在某些实施方式中，通过加入碱性材料保持溶液的pH，所述碱性材料包括水可溶性和／或水可分散性碱，例如氢氧化钠、碳酸钠、氢氧化钾、氢氧化铵、氨、和／或胺例如三乙胺、甲基乙胺、或其混合物。

[0046] 在某些实施方式中，预处理组合物还可包含树脂粘合剂。合适的树脂包括一种或多种烷醇胺与含有至少两个环氧基团的环氧官能材料的反应产物，例如描述于美国专利号5,653,823中的那些。在某些情况下，这种树脂含有β羟基酯，酰亚胺，或硫醚官能度，其通过将二羟甲基丙酸、领苯二甲酰亚胺、或巯基甘油用作在树脂的制备中的额外的反应物来引入。备选地，反应产物是摩尔比为0.6-5.0:0.05-5.5:1的双酚A的二缩水甘油醚(作为EPON880商购自Shell Chemical Company)、二羟甲基丙酸、和二乙醇胺。其它合适的树脂粘合剂包括如美国专利号3,912,548和5,328,525中所公开的水可溶性和水可分散性聚丙烯酸；如美国专利号5,662,746中所描述的酚醛树脂；水可溶性聚酰胺例如描述于WO95/33869中的那些；如加拿大专利申请2,087,352中所描述的马来酸或丙烯酸与烯丙醚的共聚物；以及水可溶性和可分散性树脂包括如美国专利号5,449,415中所讨论的环氧树脂、氨基塑料、酚醛树脂、鞣酸、和聚乙烯基苯酚。

[0047] 在本发明的这些实施方式中，树脂粘合剂基于所述组合物中成分的总重量计经常可以以0.005重量％-30重量％，例如0.5-3重量％的量存在于所述预处理组合物中。

[0048] 然而，在其它实施方式中，预处理组合物可基本上不含或，在某些情况下，完全不含任何树脂粘合剂。本文使用的术语“基本上不含”，当参照在预处理组合物中不存在树脂粘合剂使用时，是指任何树脂粘合剂是以少于0.005重量％的痕量存在于所述预处理组合物中。本文使用的术语“完全不含”是指在预处理组合物中完全没有树脂粘合剂。

[0049] 预处理组合物可任选地含有其它材料例如常规地用于预处理的领域中非离子表面活性剂和助剂。在水介质中，可以存在水可分散性有机溶剂，例如，有至多约8个碳原子的醇例如甲醇、异丙醇等；或二醇醚例如乙二醇、二乙二醇、或丙二醇等的单烷基醚。当存在时，水可分散性有机溶剂基于所述水介质的总体积计典型地以至多约10体积％的量使用。

[0050] 其它任选的材料包括起到消泡剂或基材润湿剂作用的表面活性剂。可以使用阴离子、阳离子、两性，和／或非离子表面活性剂。消泡表面活性剂经常以至多1重量％，例如至多0.1重量％的水平存在，以及润湿剂典型地以至多2％，例如至多0.5重量％的水平存在，基于所述预处理组合物的总重量计。

[0051] 在某些实施方式中，预处理组合物还可包含硅烷，例如，例如，含氨基的硅烷偶联剂、其水解产物、或其聚合物，如美国专利申请公开号2004/0163736A1中第[0025]-[0031]段所述，其引述部分通过引用并入本文。然而，在本发明的其它实施方式中，预处理组合物基本上不含，或，在某些情况下，完全不含任何这种含氨基的硅烷偶联剂。本文使用的术语“基本上不含”，当参照在预处理组合物中不存在含氨基的硅烷偶联剂时，是指存在于所述预处理组合物中的任何含氨基的硅烷偶联剂、其水解产物、或其聚合物以少于5ppm的痕量存在。本文使用的术语“完全不含”是指在预处理组合物完全没有含氨基的硅烷偶联剂，其水解产物，或其聚合物。

[0052] 在某些实施方式中，预处理组合物还可包含反应加速剂，例如亚硝酸根离子、含硝基的化合物、硫酸羟胺、过硫酸根离子、亚硫酸根离子、连二亚硫酸根离子、过氧化物、铁(III)离子、柠檬酸铁化合物、溴酸根离子、高氯酸根(perchlorinate)离子、氯酸离子、亚氯酸根离子以及抗坏血酸、柠檬酸、酒石酸、丙二酸、琥珀酸及其盐。合适的材料的具体的例子和它们的用量描述于美国专利申请公开号2004/0163736A1的第[0032]-[0041]中，其所引述的部分通过引用并入本文。

[0053] 在某些实施方式中，预处理组合物基本上或，在某些情况下，完全不含磷酸根离子。本文使用的术语“基本上不含，”当参照在预处理组合物中不存在磷酸根离子使用时，是指磷酸根离子没有以这样的程度存在于所述组合物中，以使得磷酸根离子对环境造成负担。例如，磷酸根离子可以以少于10ppm的痕量存在于所述预处理组合物中。即，没有大量地使用磷酸根离子以及避免了沉淀物（例如在使用基于磷酸锌的处理剂的情况下形成的磷酸铁和磷酸锌）的形成。

[0054] 在某些实施方式中，预处理组合物还可包括磷酸根离子的源。例如，磷酸根离子可以以大于10ppm到至多60ppm，例如20ppm-40ppm或例如30ppm的量添加。

[0055] 在某些实施方式中，预处理组合物基本上，或在某些情况下，完全不含铬酸盐。本文使用的术语“基本上不含，”当参照在预处理组合物中不存在铬酸盐使用时，是指任何铬酸盐是以少于5ppm的痕量存在于所述预处理组合物中。本文使用的术语“完全不含”，当参照在预处理组合物中不存在铬酸盐使用时，是指在预处理组合物中完全没有铬酸盐。

[0056] 在某些实施方式中，预处理涂料组合物残余物的膜覆盖的通常范围为1-1000毫克每平方米(mg/m^2)，例如，10-400mg/m^2。在某些实施方式中，预处理涂层的厚度可以是少于1微米，例如1-500纳米，或10-300纳米。在与预处理溶液接触之后，基材任选地可由水冲洗并且干燥。在某些实施方式中，基材可以在烘箱中在15-200℃(60-400° F)下干燥0.5-30分钟，例如在70° F下干燥10分钟。

[0057] 任选地，在预处理步骤之后，基材可以然后与后冲洗溶液接触。通常，后冲洗溶液，使用某可溶性金属离子或其它无机材料（例如磷酸盐或简单或复杂的氟化物）来增强经预处理的金属基材的腐蚀保护。这些后冲洗溶液可以是含铬或非含铬后冲洗溶液。可用于本发明的合适的非铬后冲洗溶液公开在美国专利5,653,823；5,209,788；和5,149,382中；全部都转让给PPGIndustries, Inc，并通过引用并入本文。此外，有机材料（树脂或其它）例如亚磷酸化(phosphitized)环氧化物、碱溶性、含羧酸的聚合物，不饱和羧酸的羟基-烷基酯的至少部分中和的互聚物，和含胺盐基的树脂（例如多环氧化物和伯或仲胺的酸溶性反应产物）可以单独使用或与可溶性金属离子和/或其它无机材料结合使用。在任选的后冲洗（当使用时）后，基材可在后续加工之前由水冲洗。

[0058] 在本发明方法的某些实施方式中，在基材与预处理组合物接触后，其然后可与包含成膜树脂的涂料组合物接触。可使用任何合适的技术将基材与这样的涂料组合物接触，所述技术包括，例如，刷涂、浸涂、浇涂、喷涂等。然而，在某些实施方式中，如以下更详细的描述，这样的接触包括电涂步骤，其中可电沉积的组合物通过电沉积沉积在金属基材之上。

[0059] 本文使用的术语“成膜树脂”是指在除去存在于组合物中的任何稀释剂或载体之后或在环境或升高的温度下固化之后，可在基材的至少一个水平表面上形成自支撑连续膜的树脂。可以使用的常规的成膜树脂包括，且不限于，典型地用于汽车OEM涂料组合物、汽

车修补涂料组合物、工业涂料组合物、建筑涂料组合物、卷材涂料组合物、和航空航天涂料组合物等的那些。

[0060] 在某些实施方式中，涂料组合物包含热固性成膜树脂。本文使用的术语“热固性”是指在固化或交联之后不可逆转地“固化”的树脂，其中聚合型组分的聚合物链通过共价键连接在一起。该性质通常与经常引发（例如，通过热或辐射）的组合物成分的交联反应相联系。固化或交联反应还可在环境条件下进行。一旦固化或交联后，热固性树脂在施加热之后不会熔化并且在溶剂中是不可溶的。在其它实施方式中，涂料组合物包含热塑性成膜树脂。本文使用的术语“热塑性”是指树脂包含不是由共价键连接的聚合型组分并且由此在加热后可进行液体流动并且在溶剂中可溶。

[0061] 如之前所述，在某些实施方式中，通过电涂步骤（其中可电沉积的组合物通过电沉积沉积在金属基材之上）将基材与包含成膜树脂的涂料组合物接触。在电沉积的工艺中，金属基材经处理，充当电极，和导电性对电极置于与离子，可电沉积的组合物接触。在电极和对电极之间的电流导通之后，虽然它们与可电沉积的组合物接触，但是可电沉积的组合物的粘附膜将以基本连续的方式沉积在金属基材上。

[0062] 电沉积通常在 1 伏特 - 几千伏特，典型地为 50-500 伏特的范围内的恒电压下进行。在电沉积工艺期间中，电流密度通常为约 1.0 安培 -15 安培每平方英尺（10.8-161.5 安培每平方米）并且倾向于快速降低，表明形成了连续的自绝缘膜。

[0063] 在本发明某些实施方式中使用的可电沉积的组合物经常包含分散在水介质中的树脂相，其中所述树脂相包含：(a) 含活泼氢基团的离子可电沉积的树脂，和 (b) 具有与 (a) 活泼氢基团有反应性的官能团的固化剂。

[0064] 在某些实施方式中，在本发明某些实施方式中使用的可电沉积的组合物含有，作为主要成膜聚合物的含活泼氢的离子的（经常是阳离子）可电沉积的树脂。许多种可电沉积的成膜树脂是已知的并且可用 z 本发明中，只要所述聚合物是“可水分散的”，即，经适应以在水中溶解、分散或乳化。水可分散性聚合物在本质上是离子的，即，所述聚合物含有赋予负电荷的阴离子官能团或，赋予正电荷的阳离子官能团，这经常是优选的。

[0065] 适用于阴离子可电沉积组合物的成膜树脂的例子是碱溶性、含羧酸的聚合物，例如干性油或半干性脂肪酸酯与二羧酸或酸酐的反应产物或加合物；和脂肪酸酯、不饱和酸或酸酐以及任何额外的进一步与多元醇反应的不饱和改性材料的反应产物。还合适的是不饱和羧酸的羟基 - 烷基酯、不饱和羧酸和至少一种其它烯属不饱和单体的至少部分中和的互聚物。仍其它合适的可电沉积的成膜树脂包含醇酸 - 氨基塑料载体 (vehicle)，即，含有醇酸树脂和胺 - 醛树脂的载体。仍另一种阴离子可电沉积的树脂组合物包含树脂型多元醇的混合酯，例如描述于美国专利号 3,749,657 中第 9 栏，第 1-75 行和第 10 栏，第 1-13 行，其所引述的部分通过引用并入本文。还可以使用其它酸官能聚合物，例如本领域技术人员已知的磷酸化多环氧化物或磷酸化丙烯酸类聚合物。

[0066] 如上所述，经常期望含活泼氢的离子可电沉积的树脂 (a) 是阳离子的并且能够在阴极上沉积。这种阳离子成膜树脂的例子包括含胺盐基团的树脂，例如多环氧化物和伯或仲胺的酸溶性反应产物，例如描述于美国专利号 3,663,389；3,984,299；3,947,338；和 3,947,339 中的那些。经常，这些含胺盐基团的树脂与封闭的异氰酸酯固化剂一起使用。所述异氰酸酯可以是完全封闭的，如美国专利号 3,984,299 中所描述的，或所述异氰酸酯可

以是部分封闭的并且可以与树脂主链反应，例如美国专利号3,947,338所描述的。同样地，如美国专利号4,134,866和DE-OS号2,707,405中所描述的一组分组合物可用作成膜树脂。除环氧化物－胺反应产物之外，成膜树脂还可选自阳离子丙烯酸类树脂，例如描述于美国专利号3,455,806和3,928,157中的那些。

[0067] 除含胺盐基团的树脂之外，还可以采用含季铵盐基团的树脂，例如美国专利号3,962,165；3,975,346；和4,001,101中所描述的通过将有机多环氧化物与叔胺盐反应而形成的那些。其它阳离子树脂的例子是含叔锍盐基团的树脂和含季鏻盐基团的树脂，例如分别描述于美国专利号3,793,278和3,984,922中的那些。同样地，可以使用经由酯基转移固化的成膜树脂，例如在欧洲专利号12463中所描述的。进一步，可以使用由曼尼希碱制备的阳离子组合物，例如在美国专利号4,134,932中所描述的。

[0068] 在某些实施方式中，存在于所述可电沉积的组合物中的树脂是带正电荷的含有伯和／或仲胺基的树脂，例如在美国专利号3,663,389；3,947,339；和4,116,900中所描述的。在美国专利号3,947,339中，多胺的多酮亚胺衍生物（例如二亚乙基三氨或三亚乙基四胺）与多环氧化物反应。当用酸中和反应产物并分散于水中时，产生了游离伯胺基团。同样地，当多环氧化物与过量的多胺（例如二亚乙基三胺和三亚乙基四胺）反应并将过量的多胺从反应混合物中真空汽提时，形成了等价产物，如美国专利号3,663,389和4,116,900所描述的。

[0069] 在某些实施方式中，含活泼氢的离子可电沉积的树脂基于电沉积槽的总重量计以1-60重量％，例如5-25重量％的量存在于所述可电沉积的组合物中。

[0070] 如上所述，可电沉积的组合物的树脂相经常进一步包含固化剂，其经适应以与离子可电沉积的树脂的活泼氢基团反应。例如，封闭的有机多异氰酸酯和氨基塑料固化剂均适用于本发明，但是封闭的异氰酸酯经常优选用作阴极电沉积。

[0071] 氨基塑料树脂（其是用于阴离子电沉积的经常优选的固化剂）是胺或酰胺与醛的缩合产物。合适的胺或酰胺的例子是三聚氰胺，苯并胍胺，脲和类似的化合物。通常，采用的醛是甲醛，但是可以由其它醛制备产物，例如乙醛和糠醛。所述缩合产物取决于采用的特定的醛含有羟甲基或类似的烷基醇基。经常，这些羟甲基通过与醇（例如含1-4个碳原子的一元醇，例如甲醇、乙醇、异丙醇和正丁醇）反应来醚化。氨基塑料树脂以商标CYMEL商购自American Cyanamid Co.以及以商标RESIMENE商购自Monsanto Chemical Co.。

[0072] 氨基塑料固化剂经常以范围为5％-60重量％，例如20％-40重量％的量与含活泼氢的阴离子可电沉积的树脂一起使用，百分比基于所述可电沉积的组合物中树脂固体的总重量计。如上所述，封闭的有机多异氰酸酯经常用作阴极电沉积组合物的固化剂。所述多异氰酸酯可以是完全封闭的，如美国专利号3,984,299在第1栏，第1-68行，第2栏，和第3栏，第1-15行所述，或部分封闭的并且与聚合物主链反应，如美国专利号3,947,338第2栏，第65-68行，第3栏，和第4栏第1-30行所述，其所引述的部分通过引用并入本文。“封闭的”是指异氰酸酯基已经与化合物反应以使得得到的封闭的异氰酸酯基在环境温度下对活泼氢是稳定的但是在升高的温度通常为90℃-200℃下与成膜聚合物的活泼氢是有反应性的。

[0073] 合适的多异氰酸酯包括芳族和脂族多异氰酸酯，包括脂环族多异氰酸酯并且代表性的例子包括二苯基甲烷-4,4'-二异氰酸酯(MDI)、2,4-或2,6-甲苯二异氰酸

酯 (TDI)，包括其混合物，对苯二异氰酸酯、四亚甲基和六亚甲基二异氰酸酯、二环己基甲烷 -4,4' - 二异氰酸酯、异佛尔酮二异氰酸酯、苯基甲烷 -4,4' - 二异氰酸酯和聚亚甲基聚苯基异氰酸酯的混合物。可以使用较高级的多异氰酸酯，例如三异氰酸酯。例子包括三苯基甲烷 -4,4',4"- 三异氰酸酯。还可以使用异氰酸酯与多元醇（例如新戊二醇和三羟甲基丙烷）以及与聚合型多元醇（例如聚己内酯二醇和三醇）(NCO/OH 当量比大于 1) 的预聚物。

[0074] 多异氰酸酯固化剂典型地以范围为 5 重量% -60 重量%，例如 20 重量% -50 重量%的量与含活泼氢的阳离子可电沉积的树脂一起使用，百分比基于所述可电沉积的组合物中树脂固体的总重量计。

[0075] 在某些实施方式中，包含成膜树脂的涂料组合物还包含钇。在某些实施方式中，钇以 10-10,000ppm，例如不大于 5,000ppm，以及，在某些情况下，不大于 1,000ppm 总钇（以元素钇测量）的量存在于这种组合物中。可溶和不可溶的钇化合物均可充当钇的源。适用于不含铅的可电沉积的涂料组合物的钇源的例子是可溶性有机和无机钇盐例如乙酸钇、氯化钇、甲酸钇、碳酸钇、氨基磺酸钇、乳酸钇和硝酸钇。当钇作为水溶液加入电涂槽时，硝酸钇（容易获得的钇化合物）是优选的钇源。适用于可电沉积的组合物的其它钇化合物是有机和无机钇化合物例如氧化钇、溴化钇、氢氧化钇、钼酸钇、硫酸钇、硅酸钇、和草酸钇。还可以使用有机钇络合物和钇金属。当钇作为颜料糊料的组分被引入电涂槽中时，氧化钇经常是优选的钇源。

[0076] 本文描述的可电沉积的组合物是水分散体的形式。术语“分散体”据信是两相透明、半透明或不透明树脂体系，其中树脂是在分散相中并且水是在连续相中。树脂相的平均粒度通常小于 1.0 并且通常小于 0.5 微米，经常小于 0.15 微米。

[0077] 水介质中树脂相的浓度基于所述水分散体的总重量计经常是至少 1 重量%，例如 2-60 重量%。当这种组合物是树脂浓缩物的形式时，它们基于所述水分散体的总重量计通常具有 20-60 重量%的树脂固体含量。

[0078] 本文描述的可电沉积的组合物经常作为双组分提供 :(1) 澄清的树脂进料，其通常包括含活泼氢的离子可电沉积的树脂，即，主要成膜聚合物、固化剂、和任何额外的水可分散的非颜料组分 ;和 (2) 颜料糊料，其通常包括一种或多种着色剂（如下描述），水可分散的研磨型树脂，其可以与主要的成膜聚合物相同或不同，以及任选地添加剂例如润湿助剂或分散助剂。电沉积槽组分 (1) 和 (2) 分散在水介质中，其包含水以及，通常，聚结溶剂。

[0079] 如上所述，除水之外，水介质可含有聚结溶剂。可用的聚结溶剂经常是烃、醇、酯、醚和酮。优选的聚结溶剂经常是醇、多元醇和酮。具体的聚结溶剂包括异丙醇、丁醇、2- 乙基己醇，异佛尔酮，2- 甲氧基戊酮，乙二醇和丙二醇以及乙二醇的单乙基单丁基和单己基醚。聚结溶剂的量基于所述水介质的总重量计通常为 0.01-25%，例如 0.05-5 重量%。

[0080] 此外，着色剂以及，如果期望的话，各种添加剂例如表面活性剂、润湿剂或催化剂可包括在含成膜树脂的涂料组合物中。本文使用的术语“着色剂”是指将颜色和 / 或其它不透明性和 / 或其它目视效果赋予组合物的任何物质。着色剂可以以任何合适的形式（例如分离的颗粒、分散体、溶液和 / 或薄片）添加至组合物中。可以使用单一着色剂或两种或更多种着色剂的混合物。

[0081] 着色剂的例子包括颜料、染料和染料剂，例如用于涂料工业和 / 或列于 Dry Color Manufacturers Association(DCMA)，以及特殊效果组合物中的那些。着色剂可包括，例如，

在使用条件下不可溶但可湿的细分的固体粉末。着色剂可以是有机或无机的并且可以是团聚的或非团聚的。可通过使用研磨工具（grind vehicle)（例如丙烯酸类研磨工具）将着色剂引入，研磨工具的使用对于本领域技术人员来说是熟悉的。

[0082]　颜料和／或颜料组合物的例子包括，但不限于，咔唑二噁嗪天然颜料、偶氮、单偶氮、双偶氮、萘酚 AS、盐型（色淀）、苯并咪唑酮、缩合物、金属络合物、异吲哚酮、异吲哚啉和多环酞菁、喹吖啶酮、二萘嵌苯、紫环酮、二酮吡咯并吡咯、硫靛、蒽醌、靛蒽醌、蒽素嘧啶、黄烷士酮、皮蒽酮、蒽垛蒽酮、二噁嗪、三芳基碳鎓、喹酞酮颜料、二酮吡咯并吡咯红（“DPPBO红”）、二氧化钛、炭黑和它们的混合物。术语“颜料”和“着色的填料”可以互换地使用。

[0083]　染料的例子包括，但不限于，是溶剂和／或基于水的那些，例如酞菁绿或蓝、氧化铁、钒酸铋、蒽醌、二萘嵌苯、铝和喹吖啶酮。

[0084]　染料剂的例子包括，但不限于，分散于基于水的或水可混溶的载体的颜料，例如商购自 Degussa, Inc. 的 AQUA-CHEM 896，商购自 Eastman Chemical, Inc 的 Accurate Dispersion 分部的 CHARISMA 着色剂和 MAXITONER INDUSTRIAL 着色剂。

[0085]　如上所述，着色剂可以是分散体的形式，所述形式包括，但不限于，纳米颗粒分散体。纳米颗粒分散体可包括产生期望的目视颜色和／或不透明性和／或目视效果的一种或多种高度分散的纳米颗粒着色剂和／或着色剂颗粒。纳米颗粒分散体可包括着色剂，例如具有小于 150nm，例如小于 70nm，或小于 30nm 的粒度的颜料或染料。纳米颗粒可通过用具有小于 0.5mm 的粒度的研磨介质研磨原料有机或无机颜料来制备。纳米颗粒分散体的例子和制备它们的方法描述于美国专利号 6,875,800B2 中，其通过引用并入本文。纳米颗粒分散体还可通过结晶、沉淀、气相冷凝、和化学磨损（即，部分溶解）来制备。为了最小化涂料内纳米颗粒的再团聚，可以使用树脂涂覆的纳米颗粒的分散体。本文使用的“树脂涂覆的纳米颗粒的分散体”是指在其中分散了离散的“复合微粒”的连续相，所述复合微粒包含纳米颗粒和在纳米颗粒上的树脂涂料。树脂涂覆的纳米颗粒的分散体的例子和制备它们的方法描述于 2004 年 6 月 24 日提交的美国专利申请公开号 2005-0287348A1，2003 年 6 月 24 日提交的美国临时申请号 60/482,167，和 2006 年 2 月 20 日提交的美国专利申请序列号 11/337,062，其也通过引用并入本文。

[0086]　可以使用的特殊效果组合物的例子包括产生一种或多种外观效应例如反射率、珠光性、金属光泽、磷光性、荧光性、光致变色性、光敏性、热致变色性、随角异色(goniochromism) 和／或颜色改变的颜料和／或组合物。另外的特殊效果组合物可提供其它可察觉的性质，例如不透明性或纹理。在某些实施方式中，特殊效果组合物可产生色移，以使得当以不同角度观察涂层时，涂层颜色改变。颜色效果组合物的例子描述于美国专利号 6,894,086 中，其通过引用并入本文。另外的颜色效果组合物可包括透明涂覆的云母和／或合成的云母、经涂覆的二氧化硅、经涂覆的氧化铝、透明的液晶颜料、液晶涂料和／或其中干涉由材料内的折射指数差异引起而不是由于材料表面和空气之间的折射指数差异的任何组合物。

[0087]　在某些实施方式中，可以使用当暴露于一种或多种光源时可逆地改变其颜色的光敏组合物和／或光致变色组合物。光致变色和／或光敏组合物可通过暴露于特定的波长来活化。当组合物受到激发时，分子结构改变并且该改变的结构显示出不同于组合物的原始

颜色的新的颜色。当移除对辐射的暴露时，光致变色和/或光敏组合物可恢复到静态，其中恢复组合物的原始颜色。在某些实施方式中，光致变色和/或光敏组合物在非激发态下是无色的并且在激发态显示出颜色。完全的颜色改变可在几毫秒至几分钟内，例如 20 秒 -60 秒内出现。光致变色和/或光敏组合物的例子包括光致变色染料。

[0088] 在某些实施方式中，光敏组合物和/或光致变色组合物可与聚合物和/或可聚合组分的聚合型材料关联和/或至少部分键连，例如通过共价键合。与其中光敏组合物可以迁移出涂料并且结晶到基材中的一些涂料相反，根据本发明的某些实施方式与聚合物和/或可聚合的组分关联和/或至少部分键连的光敏组合物和/或光致变色组合物，具有最小的迁移出涂料的量。光敏组合物和/或光致变色组合物的例子和制备它们的方法描述于 2004 年 7 月 16 日提交的美国专利申请序列号 10/892,919 中，其通过引用并入本文。

[0089] 通常，着色剂可以以足以赋予期望的目视和/或颜色效果的任意量存在于涂料组合物中。着色剂可占 1-65 重量%，例如 3-40 重量%或 5-35 重量%，且重量%基于所述组合物的总重量计。

[0090] 在沉积之后，经常加热涂层以固化沉积的组合物。加热或固化操作经常在范围为 120-250℃，例如 120-190℃的温度下进行 10-60 分钟。在某些实施方式中，得到的膜的厚度为 10-50 微米。

[0091] 如通过之前描述所领会的，本发明涉及用于处理金属基材的组合物。这些组合物包含：第 IIIB 族和/或第 IVB 族金属；游离氟离子；和锂。所述组合物，在某些实施方式中，基本上不含重金属磷酸盐，例如磷酸锌和含镍的磷酸盐，和铬酸盐。

[0092] 如通过之前描述所指出的，在某些实施方式中，本发明的方法和经涂覆的基材包括晶态磷酸盐，例如磷酸锌、或铬酸盐的沉积。因此，可以避免与这种材料相关的环境缺点。然而，已经表明本发明的方法提供了经涂覆的基材，在至少一些情况下，其耐腐性的水平类似于，在某些情况下甚至优于，其中使用这种材料的方法。这是本发明的惊人和未预料到的发现并且满足本领域的长期需求。

[0093] 以下实施例说明了本发明，所述实施例不能被认为将本发明限制到它们的细节。除非另有指示，否则实施例以及说明书中的所有份数和百分比是以重量计的。

[0094] 实施例 1

[0095] 通过用 Chemkleen 166M/Chemkleen 171/11（得自 PPG Industries 的双组份液体碱性清洁剂）的溶液浸涂将十二块冷轧钢 (CRS) 板（板 1-12）在 60℃下清洁三分钟。在碱性清洁之后，用去离子水彻底地冲洗该板然后用含 0.25g/lZirco 冲洗添加剂（商购自 PPG Industries，Quattordio，Italy）的去离子水冲洗该板。

[0096] 将这些板（板 1-6）中的六个在环境温度下在锆预处理溶液中浸没两分钟，在表 2 和 3 中标示为“预处理 A”。通过用大约 400 升去离子水将 4.5 升 Zircobond ZC（含六氟锆酸铜的试剂，商购自 PPG Industries，Quattordio，Italy）稀释至锆浓度为 175ppm（作为锆）并且用 Chemfill Buffer/M（温和的碱性缓冲剂，商购自 PPG Industries，Quattordio，Italy）将 pH 调节至 4.5 来制备预处理 A。

[0097] 在预处理预处理 A 的溶液之后，板 1-6 用含有 0.25g/lZirco 冲洗添加剂的去离子水冲洗，然后用去离子水彻底得冲洗，以及然后在 70℃下在烘箱中干燥 10 分钟。板 1-6 具有浅铜色的外观并且使用便携式 X 射线荧光仪 (XRF) 测量的涂层厚度为大约 39nm。

[0098] 通过将1g/l硝酸锂（得自Sigma Aldrich code 227986）添加到预处理A溶液中以便获得100ppm锂的浓度来制备在表2中被称作“预处理B”的预处理溶液。每个板通过将其置于烘箱中在70℃下干燥大约十分钟。通过XRF测量的涂层厚度为大约39nm。

[0099] 所有用预处理A或预处理B预处理的板随后用G6MC2涂覆，G6MC2是商购自PPG Industries的含钇的阴极电涂，其含有422g树脂(W7827，商购自PPG Industries，Inc.)，98g糊剂(P9757，商购自PPG Industries，Inc.)，和480g水。根据生产商的指示制备和涂覆G6MC3涂覆槽。根据生产商的说明书固化该板。

[0100] 在固化之后，使由预处理A预处理的三个经涂覆板以及由预处理B预处理的三个经涂覆的板经受VW循环腐蚀测试PV1210。在划线和第一次抗石击之后，将所述由预处理A预处理的三个经涂覆的板以及所述由预处理B预处理的三个经涂覆的板在冷凝湿度(4小时NSS在35℃然后4小时在23℃和50％湿度，接着16小时在40℃和100％湿度）下暴露30天，以及然而在经暴露的板上进行第二VW循环腐蚀PV1210测试。以0-5的范围评级抗石击结果，其中5表示完全涂料损耗，以及0表示完美的涂料附着。在暴露于湿度之后，测量了沿着划线的腐蚀蠕变和抗石击的结果。

[0101] 使由预处理A处理的剩余的三个经涂覆的板和由预处理B处理的剩余的三个经涂覆的板经受GM循环腐蚀测试，其中通过切入涂料系统直到金属对该板划线。将该板在冷凝湿度(8小时在25℃和45％湿度然后8小时在49℃和100％湿度接着8小时在60℃和30％湿度）下暴露40天。在测试的结尾，通过测量来自划线（蠕变）的涂料损失和以毫米计算的每个板的最大的蠕变（两侧）对该板评级。结果总结于下表2中

[0102] 使用飞行时间次级离子质谱法(ToF-SIMS)测试由预处理B处理的板上的膜，ToF-SIMS表明该膜由锆、氧、氟离子、和锂组成。锂存在于整个膜中。

[0103] 表2

[0104]

预处理	电涂	2次循环 GMW 14872 测试	30次循环VW PV1210 测试	
		沿着划线的腐蚀(mm)	沿着划线的腐蚀(mm)	抗石击蠕变评级[
A	G6MC3	9.5	1.2	4.0
B	G6MC3	6.3	0.8	3.0

[0105] 实施例2

[0106] 如实施例1预处理冷轧钢板，且一半的板用预处理A预处理并且另一半用“预处理C”预处理，其中通过将硝酸锂和钼酸钠添加到预处理A中以便获得40ppm钼和100ppm锂的浓度来制备预处理C。每个板通过将其置于烘箱中在70℃下干燥大约十分钟。由XRF测量的涂层厚度为大约40nm。

[0107] 随后用ED6070/2电涂该板，ED6070/2是商购自PPG Industries的含钇的阴极电涂，其含有472g树脂(W7910，商购自PPG Industries，Inc.)，80g糊剂(P9711，商购自PPG Industries，Inc.)，和448g水。使该板经受VW循环腐蚀测试PV1210。结果显示在下表3中。

[0108] 使用ToF-SIMS，X射线光电子能谱(XPS)，和X射线荧光光谱(XRF)测试由预处理C预处理的板上的膜。ToF-SIMS表明锂和钼存在于整个涂层中并且钼以混合氧化物形式存

在。XPS 和 XRF 证实钼存在，占氧化锆膜重量的 1-10％。锆、氧、氟离子、锂、和钼存在于该膜中。

[0109] 表 3

[0110]

预处理	电涂	30 次循环 VW PV1210 测试	
		沿着划线的腐蚀(mm)	抗石击蠕变评级
A	ED6070/2	0.75	2.5
C	ED6070/2	0.5	2

[0111] 本领域技术人员应领会在没有背离本发明宽泛概念的情况下，可以做出上述实施方式的改变。因此，应理解本发明不限制于所公开的特定的实施方式，但其旨在覆盖在本发明精神和范围内的改变，如所附权利要求所限定的。